The History of Vacuum Coating Technologies

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About the Author

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The author encourages readers to provide comments, corrections, and/or additions, and would like to be made aware of any historical references not given in this work. Copies of such references would be appreciated.

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Introduction

Vacuum coatings processes use a vacuum (sub-atmospheric pressure) environment and an atomic or molecular condensable vapor source to deposit thin films and coatings. The vacuum environment is used not only to reduce gas particle density but also to limit gaseous contamination, establish partial pressures of inert and reactive gases, and control gas flow. The vapor source may be from a solid or liquid surface (physical vapor deposition—PVD), or from a chemical vapor precursor (chemical vapor deposition—CVD). The terms "physical vapor deposition" and "chemical vapor deposition" seem to have originated with C.F. Powell, J.H. Oxley, and J.M. Blocher, Jr., in their 1966 book Vapor Deposition to differentiate between the types of vapor sources [1]. The term "vacuum deposition" is often used instead of PVD, particularly in the older literature such as Leslie Holland's classic 1961 book Vacuum Deposition of Thin Films [2]. Vacuum coatings can also be formed by deposition of molten particles in a vacuum [2a], but that process will not covered in this article.

In PVD processing the vaporization may be from thermal heating of a solid (sublime) or liquid (evaporate) surface or by the non-thermal (momentum transfer) process of sputtering (physical sputtering). When the depositing material reacts with the ambient gaseous environment or a co-deposited material to form a compound, it is called reactive deposition. If the vapor source is from a solid molecular species (such as silicon-oxide), some of the more volatile constituents may be lost upon vaporization. If these lost species are replaced by a reactive species from the deposition environment, the process may be called quasi-reactive deposition. The particle density in the vacuum may be such as to sustain a plasma discharge that provides ions and electrons. This plasma "activates" reactive gases for reactive deposition processes and aids in the decomposition of chemical vapor precursors ("plasma deposition" or plasma-enhanced chemical vapor deposition—PECVD). In some cases PVD and CVD processes are combined to deposit the material in a "hybrid process." For example, the deposition of titanium carbonitride (TiCxNy or Ti(CN)) may be performed using a hybrid process where the titanium may come from sputtering; the nitrogen is from a gas and the carbon from acetylene vapor. Alloys, compounds and composite materials can be deposited using a single source of the desired material or multiple sources of the constituents.

In many instances the term "thin film" is used when discussing PVD vacuum deposits. This is because most early applications did not rely on the mechanical properties of the deposited material; they relied on the optical and electrical properties of thin deposits. In many recent applications the vacuum-deposited materials have been used for mechanical, electrical, and tribological applications, and the deposit thickness has become greater. The term "thick films" is not appropriate because that term is used for paint-on, fire-on coatings from slurries [3]. The term "metallurgical coating" is sometimes used but would not seem to be applicable to coatings that are not metallic. So the term "vacuum coating" is used here to refer to both thin films and thick deposits deposited by PVD or CVD is a sub-atmospheric (vacuum) gaseous environment. As an arbitrary delineation, the term "thin film" will generally be used for deposits less than about 0.5 microns (5,000 Ångstroms or 500 nanometers) in thickness. This type of vacuum coating process is not to be confused with the "vacuum coating" process in the paint industry where excess paint is removed from a moving surface by a "vacuum."

The history of vacuum coating processes is closely associated with the history and development of vacuum technology, electricity, magnetism, gaseous chemistry, plasma technology, thermal evaporation, arcing, and sputtering. "Pioneering" work (F-1) in these areas has led to many advancements in vacuum coating technology.

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Early Vacuum Science and Technology [4-8]

In about 1640, Otto von Guericke made the first piston-type vacuum pump (he called them “air pumps”) patterned after the water pumps that had been used for many years to remove water from mines [9]. Figure 1 shows a woodcut picture of a mine being pumped out using several stages of water pumps. In 1654 von Guericke performed the famous “Magdeberg hemispheres” demonstration that really introduced the vacuum pump to the scientific world. In 1643 Torricelli demonstrated the mercury barometer based on the water manometer experiments of Berti (~1640). In 1662 Boyle formulated Boyle’s Law, and in 1801 Dalton expressed the Law of Partial Pressures. Piston-type vacuum pumps came into widespread use, but vacuum experiments had to be continually pumped because of the poor vacuum seals available at that time.

In the early to mid-1800s, heat-moldable, electrically insulating materials included gutta-percha, a material made from the sap of a tree native to Southeast Asia (F. Montgomery brought to Europe, 1843); the molded plastic made from shellac and sawdust (and later coal dust) (H. Peck & C. Halvorson, Norway, 1850); and “India rubber,” which was made from rubber tree sap, sulfur, and gum shellac (G. Goodyear, 1851). L. Baekeland invented “Bakelite,” the first totally synthetic thermosetting plastic, in 1907. Glass-forming (ancient) and porcelain fabrication (W. Bottger, Germany, 1710) were well understood by the mid-1800s.

In 1857 H. Geissler invented the platinum-to-glass seal that allowed sealed-off vacuum tubes to be produced. This was a major advance in vacuum technology. Neoprene (“artificial”) rubber was invented by DuPont in 1933, and molded seals of this material began to be used by the vacuum community in the late 1930s and replaced wax sealing. As late as the 1960s, finding and fixing vacuum leaks was a major part of vacuum technology and “Glyptol” (a paint—GE), “black wax” (Apiezon—W) and “elephant s—” (a putty) (Apiezon—Q) were common fixtures in the vacuum facility. Many of the early experiments used hydrogen flushing to augment vacuum pumping to reduce oxygen in the chamber. During WWII the Germans used phosphorus pentoxide, a desiccant, in the vacuum chamber to remove water vapor when depositing optical coatings.

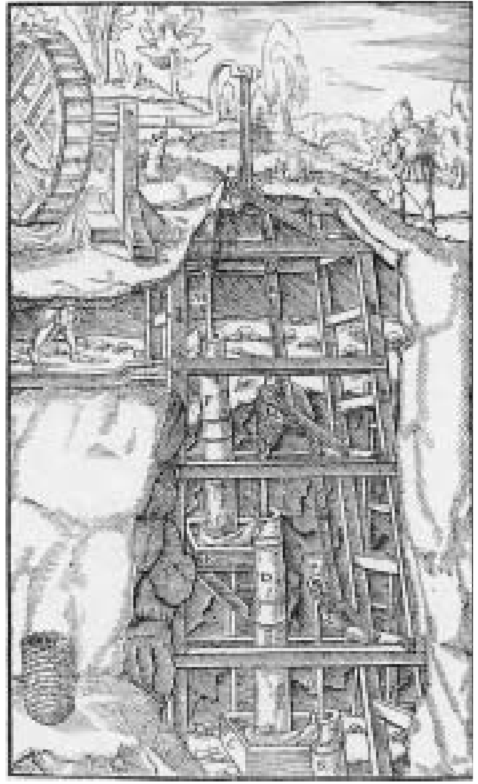

Figure 1. Multistage “syringe” water pumps removing water from a mine. From the book on mining “De Re Metallica” (1556) [9].

In 1855 H. Geissler invented the mercury piston pump, which was widely used but left mercury vapor contamination in the vacuum (mercury has a vapor pressure of 1.2 mTorr at room temperature). Töpler improved the Geissler pump, and in 1865 Sprengel invented the mercury siphon pump, which greatly reduced the labor and attention required for vacuum pumping. In 1874 McLeod invented the “McLeod vacuum gauge,” which was capable of measuring very low pressures. By using a combination of Geissler and Sprengel vacuum pumps, cold trapping and “flaming,” good vacuums (about 10^{-6} atmospheres) could be achieved. Thomas Edison used this combination of techniques in the production of the first carbon-filament electric light bulbs in 1879. Figure 2 shows vacuum pumping, 1880 style. It was not until about 1895 that liquefied air was used to trap mercury vapor pumps. This was after T. Linde and J. Hampson had introduced “regenerative cooling” as a means of liquefying gases and J. Dewar invented a means for storing liquefied gases (Dewar flask). In 1901 H.C. Booth invented the first electrically driven vacuum cleaner. The term “vacuum cleaner” was first used in Booth’s advertisements.

In 1907 W. Gaede invented the oil-sealed rotary vane mechanical pump. By 1910, electric-motor-driven oil-sealed rotary vane pumps were in common use. In 1913 the mercury diffusion pump was invented by I.

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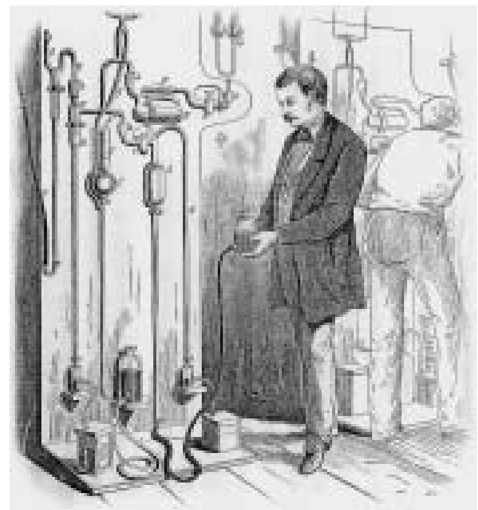

Figure 2. Vacuum pumping, 1880s style. This type of vacuum pumping system was used by T. Edison in the early manufacture of light bulbs.

Langmuir and was improved by W. Gaede in 1922. In 1926 C.R. Burch replaced the mercury with low-vapor pressure oil, though well-trapped mercury diffusion pumps were considered the "cleanest" high-vacuum pumps for many years afterward. In 1937 L. Malter built the first metal oil diffusion pump; until that time fractionating and non-fractionating diffusion pumps were made of glass. The oil diffusion pump ("diff pump") has remained the principal high-vacuum pump used on many large vacuum coating systems. During WWII, the company Distillation Products, Inc. (later Consolidated Vacuum Corp.—CVC) and National Research Corporation (NRC—later a division of Varian Corp.) were the major suppliers of vacuum equipment to the vacuum coating industry.

Cryopumps and turbomolecular pumps have widespread use in the vacuum coating industry where small chambers are pumped or where oil contamination is a major concern. The cryopump developed from the use of cold traps in vacuum chambers and also cold shrouds in space simulators [10]. Liquid helium cooling developed after the invention of the "closed-loop" helium cryostat (Gifford-McMahon cycle) in 1960 but did not come into widespread use until 1980, when Varian Corp. began marketing cryopumps. W. Gaede invented a turbopump in 1912, but the modern vertical-axis, high-RPM turbopump was developed independently in 1958 by H.A. Steinhertz and by W. Becker. Pfeiffer Corp. began marketing turbopumps in 1958.

In the mid-1990s molecular drag stages were added to turbomolecular pumps. This technology allowed turbopumps to exhaust to higher pressures so diaphragm pumps could be used as backing pumps. This combination allowed very oil-free pumping systems ("dry pumps") to be developed for critical applications. The use of piston pumps also returned due to the need for clean, dry pumps. Ultra-clean vacuum components (and their packaging) and vacuum systems were developed for the semiconductor industry around the late 1960s [11].

In 1906 W. Voege invented the thermocouple vacuum gauge, and M. von Pirani invented the Pirani gauge in 1909. That year the hot cathode ionization gauge was invented by Von Baeyer. The modern Bayard-Alpert hot cathode ionization gauge was invented by R.T. Bayard and D. Alpert in 1950. W. Sutherland (1897), I. Langmuir (1913), and J.W. Beams (1960) advanced the concept of various viscosity (molecular drag, spinning rotor) gauges. Beams' high-speed rotor work was the basis of the modern spinning rotor (molecular drag) gauge. The modern capacitance manometer gauge was invented by A.R. Olsen and L.L. Hirst in 1929 but did not become commercially available until 1961 when MKS Corporation began marketing it. F.M. Penning invented the magnetron cold cathode ionization gauge in 1937. In 1922 S. Dushman wrote the classic book *Production and Measurement of High Vacuum*. Helium leak detectors and many advancements in vacuum technology were developed during WWII in support of the isotope separation project.

In the early years vacuum chambers were predominately single chambers, though Edison patented a dual-chamber vacuum system in the early 1900s to speed up production of light bulbs. In 1987 Applied Materials Inc. introduced the first commercial multiple-chamber "cluster tool" for semiconductor processing. This system was used mostly for sequential deposition of doped and undoped PECVD films with an intermediate plasma-etching step [12].

With the advent of reactive deposition and hybrid processing, the control of gas composition and mass flow has become an important aspect of vacuum engineering and technology. This includes partial pressure control and gas manifolding in processing chambers. Many vacuum-pressure measurement instruments cannot be used for measurement of total gas pressures in the presence of a plasma in the range of interest to many PVD processes (0.5 to 20 mTorr). Capacitance manom-

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eter gauges and spinning rotor gauges are commonly used in these applications. Differentially pumped mass spectrometers can be use to monitor and control partial pressures of gases. In 1984 a mass spectrometric feedback method of controlling the partial pressure of reactive gases in reactive sputter deposition was patented. Optical emission spectroscopy is also used to control the partial pressures of reactive gases in reactive sputter deposition. Optical emission has been used for many years to detect the "end-point" in plasma etching for semiconductor processing.

The use of vacuum equipment for deposition (and etching) processes also introduces problems associated with pumping and disposing of possibly toxic, flammable, and corrosive processing gases, as well as reactive gases used for *in situ* cleaning of the vacuum systems. Specialized vacuum equipment and *in situ* chamber plasma-etch-cleaning techniques have been developed to address these concerns.

The term "vacuum" should be used with caution because it means different things to different people. To some people the term vacuum means that the gas density is so low that the gaseous species do not affect the process or phenomena being studied. To others it means a subatmospheric gas density that should, or must, be controlled during the process or study in order to have reproducible results. For example, in Jim Lafferty's 1980 book Vacuum Arcs he makes a point of saying, "If there is an arc there is no vacuum and where there is a vacuum there is no arc" [13].

Early Electricity and Magnetism [14-16]

In 1600 W. Gilbert wrote the book De Magnete (*On The Magnet*). This book is considered to be the first scientific publication. In 1672 Otto von Guericke (of vacuum pump fame) built the first electrostatic (frictional) electricity-generating machine, which used a rotating ball of sulfur. "Friction electricity" was used for entertainment in the early years. In 1732 Gray described the conduction of electricity, and about 1745 the air capacitor (Leyden jar) was invented by von Kleist, which allowed electricity to be stored. The invention of the Leyden jar is sometimes erroneously credited to Prof. van Musschenbroek at the University of Leyden in The Netherlands. In 1749 Benjamin Franklin introduced the concept of positive and negative electricity and the conservation of charge. Franklin also introduced the word "battery" for a bank of Leyden Jars. In 1800 Alessandro Volta invented the electrolytic "voltaic pile" (later called a battery) based on the observations of "animal electricity" by Luigi Galvani (1791) and others (see Figure 3). The science of electrochemistry had its beginning at that time [17]—for example, the electrodeposition of copper (Cruikshank in1800) and electrolysis, which allowed the separation of oxygen and hydrogen from water (an accidental discovery by Nicolson and Carlyle in 1800). Napoleon Bonaparte was immediately interested and supported the construction of very large arrays of batteries, as did others. For example, the Russians built an array of 4,200 Cu-Zn cells in 1803 at St. Petersburgh'sMedical and Surgical Academy. In 1810 Sir Humphry Davy produced a manmade arc (from the word "arch," which is the shape of a long arc between two electrodes in air due to heating and convection) between two electrodes. He is generally credited with producing the first manmade arc though a Russian, Vasilli V. Petrov, reported the same effect in 1803.

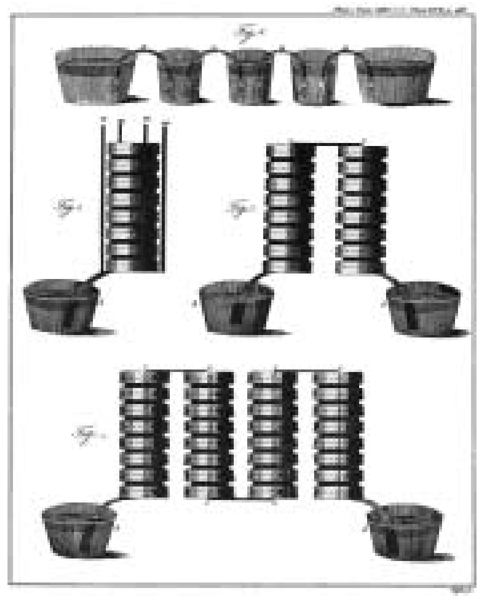

Figure 3. Four connections of "voltaic piles" (alternate silver and zinc discs separated by moist paper) as described in A. Volta's letter to Sir Joseph Banks of the Royal Society of London bearing the title "On the Electricity excited by the mere Contact of conducting Substances of different kinds," dated March 20, 1800.

In 1820 H.C. Oersted detected the magnetic field around a current-carrying wire, and in 1821 Ampére invented the galvanometer. In 1831

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Michael Faraday discovered electromagnetic induction. The first continuous generation of electricity, both AC and DC, using induction was developed by Hypolite Pixii in 1832. M. Nollet improved Pixii's design in 1849 or 1850. This led to the first commercial use of mechanically generated electricity. In 1836 N.J. Callan made the first induction coil to produce pulses of high voltages by periodically making and breaking a DC circuit. In 1851 H.D. Rühmkorff built a high-quality induction coil ("Rühmkorff coil") that allowed the generation of high voltages, and this device was widely used with gas-discharge tubes for many years.

In 1858 J. Plücker reported the bending of "cathode rays" by a magnetic field. In 1864 James Clerk Maxwell wrote the book *On a Dynamic Theory of Electromagnetic Fields*. In 1883 T. Edison placed a plate in one of his early lamp bulbs and noted that the current was higher when a filament, at a negative potential, was heated to incandescence ("Edison Effect") [18]. He was awarded a patent for the use of the changing current flow to "control machinery." In 1888 J. Elster and H. Geitel "rediscovered" the "Edison Effect," and they are often credited with discovering thermoelectron emission. In 1899 J.J. Thompson noted the same effect from a cathode of heated CaO and proposed "ionization by repeated contacts." In 1891 G.J. Stoney introduced the word "electron" for the charge passing through an electrolyte. In 1897 J.J. Thompson started his many studies on cathode rays that led to the identification of the electron (which he called a "corpuscle") in 1898. In 1895 Röntgen (or Rsntgen) discovered X-rays. In 1904 Fleming invented the "Fleming Valve," which was the forerunner of the triode vacuum tube.

Around the turn of the century there was an ongoing debate over which was better, direct current (DC) voltage advocated by Thomas Edison or alternating current (AC) voltage advocated by Nikola Tesla and George Westinghouse, who had purchased Tesla's patents (F-2). Of course AC won out partially because of its ability to step up or step down voltages using transformers. Until about the mid-1970s most high-voltage DC was produced using stepped-up voltages and electron tube rectifiers, such as the mercury vapor rectifiers. With the advent of solid-state electronics, high-voltage DC could be produced using solid-state rectifiers, but the electronics became more susceptible to arcing. RF power is used to sputter dielectric materials. Until the mid-1970s crystal-controlled oscillators were used for frequency control (13.56 MHz); after that, solid state oscillators were used. Around 1990, solid-state bipolar-pulsed power supplies became available with frequencies up to about 250 kHz (10 kHz to 250 kHz, "mid-frequency" AC) [19]. Pulsed power became an important option for sputtering and substrate biasing (F-3). High-power, mid-frequency AC power supplies could be produced at a much lower cost than comparable radio frequency (RF) power supplies.

In 1928 Thompson discovered the diffraction of electrons as they passed though a thin film. In the late 1930s an electron trap, called the "Penning discharge," in which a combination of electric and magnetic fields was used to enhance plasmas near a surface ("surface magnetron") in sputtering from cylindrical-hollow (inverted) magnetrons (F.M. Penning, 1936) and cylindrical-post magnetrons (F.M. Penning and Mobius, 1940). This was a pioneering work in sputtering. The first device called a "magnetron" was invented by Albert W. Hull in about 1920. The cavity magnetron that led to the radar of WWII was invented by H.A. Boot and J.T. Randall in 1940 [19a].

Early Plasma Physics and Chemistry [20-24]

In 1678 J. Picard noted a glow in the top of an agitated mercury barometer ("Picard's Glow"). Around 1720, F. Hawksbee used "frictional electricity" to generate a plasma in a vacuum that was intense enough "to read by." Scientists used "frictional electricity" to study the chemistry in electric sparks and plasmas before 1800. After the invention of the voltaic battery in 1800 by A. Volta, the study of the chemistry in electric arcs rapidly developed.

Since the mid-1800s there have been a number of studies of glow discharges and the spectral emission from the glows. The first glow (gas) discharge "vacuum tube" was made by M. Faraday in 1838 using brass electrodes and a vacuum of approximately 2 Torr. In 1857 Heinrich Geissler, who was the glassblower for Professor Julius Plücker, invented the platinum-to-glass seal that allowed sealed-off glow-discharge tubes (Geissler tubes) to be produced. In 1860 J.H. Hittorf, a pupil of Plücker's, noted that "cathode rays" (electrons from the cathode) pro-

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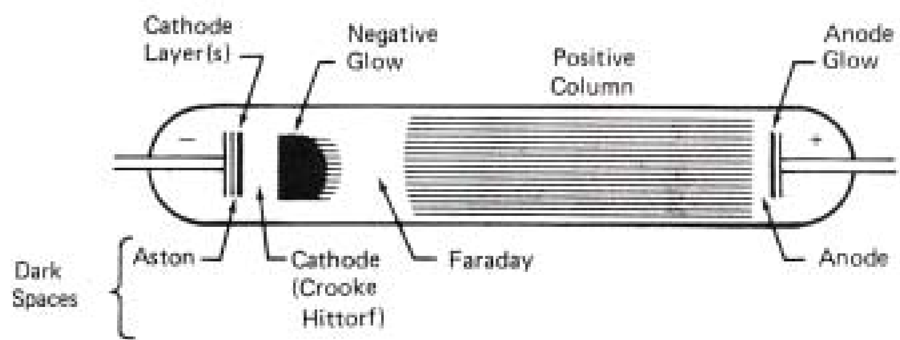

Figure 4. Glow discharge tube showing the various named region of the discharge at low pressure [24].

jected "shadows" in a gas discharge tube. In 1885 Hittorf produced an externally excited plasma ("electrodeless ring discharge") by discharging a Leyden jar through a coil outside the glass chamber. W. Crookes made a number of studies using gas discharge tubes ("Crookes' tubes"). Figure 4 shows a modern rendition of the Crookes' tube [24]. J.J. Thompson made a number of studies which indicated that the cathode ray was composed of negative particles that were the same as Stoney's "electrons." In 1886 E. Goldstein, using a perforated cathode, identified the positively charged "proton" that was about 2,000 times heavier than the electron.

In the mid-1920s I. Langmuir developed the small-area plasma probes that allowed characterization of plasmas (charge densities and particle temperatures). In 1926 Arthur R. von Hippel observed the optical emission spectra of sputtered atoms in a plasma. Although Hittorf had produced externally excited plasmas in 1885, the mechanism of this generation was in dispute until 1929 when McKinnon showed that at low gas densities the discharges were capacitively driven by coupling between the low- and high-voltage ends of the coil, while at high gas densities the plasma was inductively coupled between the turns of the coil.

In the late 1930s an electron trap, which used a combination of an electric and a magnetic field parallel to the surface called the "Penning effect," was used to enhance the plasmas near the surface in sputtering from cylindrical-hollow (inverted) magnetrons and cylindrical-post magnetrons. Work on these "surface magnetron" sputtering configurations was curtailed by WWII. The Penning effect was incorporated into a number of other applications such as vacuum gauges, sputter-ion pumps, and microwave tubes. The lifetime of plasma is determined by its contact with a solid surface. The lifetime of the plasma can be extended by using a magnetic field to prevent contact with a surface.

The first "ion guns" were developed by NASA for space propulsion. Ion sources are of two types—an ion "gun," which has an extraction grid structure and produces an ion beam with a defined ion energy and low beam dispersion, and a "broad-beam" ion source, which produces an ion beam with a large dispersion and a spectrum of ion energies (25). Research on power generation by nuclear fusion and studies of chemical synthesis in high-density plasmas accelerated the development of plasma confinement and the generation of high-density plasmas in the 1960s. These devices used electric and magnetic fields to confine and focus the plasma. Examples are the work of Gow and Ruby in 1959 [26]. Also Filipova, Filipova, and Vingredov (1962) and Mather (1964) [27] made "pinched" (focused) plasmas. These general concepts were used in the early 1970 to make "closed-loop" magnetron sputtering configurations.

The term "plasma", as we now use it, was proposed by I. Langmuir, and L. Tonks, of the General Electric Research Laboratories, in 1928,.

Scientific and Engineering Societies and Publications

The first scientific society in what became the USA was the American Philosophical Society, which was founded in 1743 under the instigation of Benjamin Franklin. The transactions of the American Philosophical Society began publication in 1771. Up to that time most American scientists published in European journals. In 1818 Benjamin Silliman, who has been called the "father of American scientific education," started publishing the American Journal of Science and Arts (F-4).

The American Vacuum Society (AVS) was formed in 1953 to provide a forum for those interested in the scientific and industrial

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development of vacuum equipment and processes [4]. At first its primary interest was vacuum melting. It was not until about the Fifth Symposium (1957) of the AVS that papers on vacuum coating began to be presented. The AVS began publishing the *Journal of Vacuum Science and Technology* in 1964. In 1974 the AVS Conference on Structure/Property Relationships in Thick Films and Bulk Coatings was held in San Francisco. The meeting was sponsored by the Vacuum Metallurgy Division of the AVS, with Roitan (Ron) Bunshah as the Program Committee Chairman. This conference became an annual event called the International Conference on Metallurgical Coatings (ICMC), and later the ICMCTF when the AVS Thin Film Division became involved. The proceedings of these meetings are published in *Thin Solid Films* and *Surface and Coating Technology*. In 2001 the American Vacuum Society became AVS—The Science and Technology Society as their interests diverged from the use of the vacuum environment.

The Society of Vacuum Coaters (SVC) was formed in 1957 to provide a forum for developments in the industrial application of vacuum coatings. The papers that were presented at the first few conferences were primarily directed toward the decorative metallizing industry. The proceedings of these conferences are published by the SVC.

Patents and the U.S. Patent Office

The existence of the U.S. Patent Office was specified by the Continental Congress in the U.S. Constitution. The first U.S. patent (#1) was issued in 1836. Until that time the patent process was very poorly organized. Up until 1880 the USPO asked for a model of the invention. Since 1880 the USPO can, but rarely does, ask for a model—an exception is a patent for a perpetual motion machine.

Patent litigation, with its high cost, has historically been used as a corporate "weapon" to spend (or threaten) people away from the use of patented work. Recently (Nov. 29, 2000) this may have changed due to a decision by the U.S. Court of Appeals in the case of *Festo Corp. v. Shoketsu Kinzoku Kogyo Kabushiki Ltd*. (234 F.3d 558, 56 USPQ2d 1865 {Fed. Cir. 2000}). This decision, which makes it harder to prove infringement on patented work, is on appeal to the U.S. Supreme Court. Basically this decision means, "Until the Supreme Court issues a decision, inventors will have to do their own extensive research before filing rather than relying on a patent examiner" ("Patent War Pending," *Amer. Bar Assoc. Journal,* Vol. 87(11), p. 28 [November 2001]).

One of the first major applications of this decision in the vacuum coating field was the dismissal of the Litton Industries patent infringement suit against Honeywell over the IBAD vacuum coating of ring laser gyro (RLG) mirrors. At one time a jury had awarded $1.2 billion to Litton and that award was under appeal when it was set aside completely by the same court that issued the Festo ruling [27a].

Deposition Processes

Sputter Deposition [28, 29]

W.R. Grove was the first to study what came to be known as "sputtering" (and sputter deposition) in 1852 [30], although others had probably previously noted the effect while studying glow discharges. Grove sputtered from the tip of a wire held very close to a highly polished silver surface (the type used for a daguerreotype) at a pressure of about 0.5 Torr, as shown in Figure 5. He noted a deposit on the silver surface when it was the anode of the circuit. The deposit had a ring structure. He made no studies on the properties of the deposited films since he was more interested in effects of voltage reversal on the discharge. In 1854 M. Faraday also reported film deposition by sputtering in a glow discharge tube. In 1858 Julius Plücker noted the formation of a platinum film inside of a discharge tube, creating a "beautiful metallic mirror" [21].

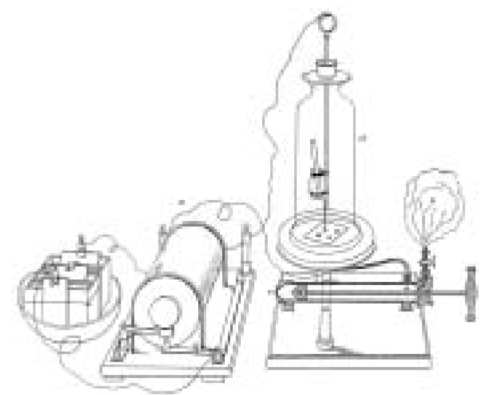

Figure 5. Grove's "sputtering" apparatus (1852) [30].

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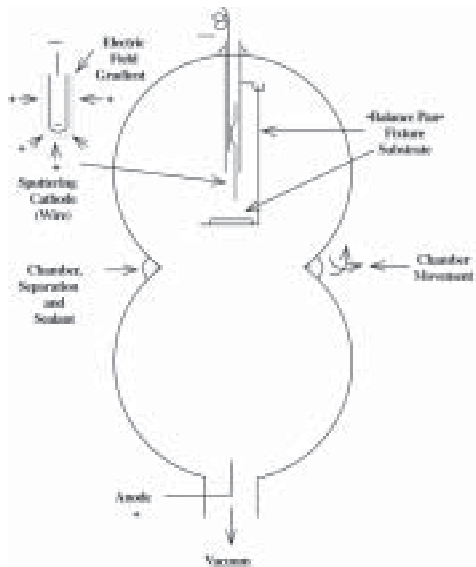

Figure 6. Wright's "electrical deposition apparatus" based on the description given in his paper (1877) [34].

In 1877 Prof. A.W. Wright of Yale University published a paper in the *American Journal of Science and Arts* (F-4) on the use of an "electrical deposition apparatus" to form mirrors and study their properties [32]. There is some confusion as to whether Wright was using sputtering or (gaseous) arcing [33], though it would seem that Wright was sputtering using an arrangement very similar to that of Grove (Figure 5) as shown in Figure 6 [34]. One major difference was that Wright used a swinging balance-pan fixture that allowed him to deposit ("paint") a film over a relatively large area rather than just at a point. Wright was not very specific in his description of the deposition process he used and the U.S. Patent Office used Wright's work as "prior art" when challenging part of T. Edison's 1884 patent application (granted 1894) on arc-based "vacuous deposition" [35]. Edison was granted his patent after maintaining that Wright's process used a "pulsed arc," whereas his was a "continuous arc." Edison also described Wright's work as a "laboratory curiosity." Professor Wright should be credited with being the first to characterize vacuum deposited films for their specific properties (color and reflectance).

In 1892 Edison used a "vacuous deposit" to "seed coat" his wax cylinder "phonogram" (phonograph) masters for subsequent electroplating [36]. In his 1902 patent on the subject [37] he indicated that the deposition process (arc deposition) described in his previous patent [35] wasn't suitable because of uniformity and heating problems, and in the figure in this patent (Figure 7) he showed a sputtering cathode (although he just called it an electrode) for depositing the metal. Edison should probably be credited with the first commercial use of sputtering. The "seed coat–electroplating" method is now used for depositing metallization on high-aspect-ratio surface features in semiconductor processing. In his 1894 patent Edison also referred to fabricating freestanding foils by stripping the deposit from the chamber walls. Edison also patented the use of sputter deposition to form freestanding foils in 1915 [38]. He was interested in making filaments for his light bulbs using this method of fabricating foils.

In 1891 W. Crookes published an article on sputtering and deposition, which he called "electrical evaporation," in the *Scientific American Supplement.* That article was probably the first "popular" publication on sputtering [39]. Crookes referred to Wright's work on producing mirrors. After the late 1800s, sputter deposition was used occasionally to make mirrors (other than silvered mirrors that were made by deposition of silver from a chemical solution) [40]. In 1912 Kohlschütter published the first comparison of the sputtering rates (sputtering yields) for various materials [41]. Later Almen and Bruce [42] made extensive studies on the sputtering yields of a number of materials. Collegon, Hicks, and Neokleous noted the variation of yield with initial target bombardment dose [43], a study that seems to rarely be noted in discussions on sputtering. In 1972 Kornelsen made several studies of gas incorporation into ion bombarded surfaces [44]. In 1963 van der Slice discussed the production of high-energy neutrals by charge-exchange processes in a glow discharge.

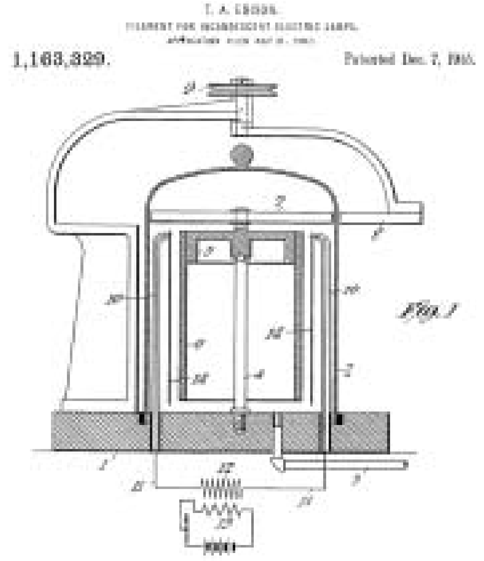

Figure 7. Edison's arrangement for coating his wax phonograph masters using a sputtering cathode (9), a high-voltage induction coil, and an external magnetically-driven, (14) rotating fixture (13) (1902) [35].

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This effect gives bombardment of the cathode, and nearby surfaces, by high-energy neutral species during sputtering [45].

The Bureau of Standards Circular #389 (1931) describes the sputter deposition of mirror coatings [46]. The circular has some interesting information on the status of vacuum materials at that time; for example, "For joint grease a special solution of crude rubber and lard was made." In the early 1930s sputter deposition onto rolls of material (web coating or roll coating) was developed. The technique was first used to deposit silver on cloth in about 1931, in Leipzig, Germany. This was quickly followed by the deposition of gold and silver on glassine (waxed paper) by K. Kurz (Germany) and C. Whiley (England) for stamping foils [47]. By the late 1930s many applications of sputtering had been replaced by the thermal evaporation process that was developed in the early to mid-1930s. In 1933 the deposition of compounds by sputtering in a reactive gas ("reactive sputter deposition") was reported by Overbeck [48] for use as optical coating though it was not widely used. The term "reactive sputtering" was introduced by Veszi in 1953 [49]. Reactive sputter deposition of tantalum nitride for thin film resistors was an early application. Tantalum nitride has about the same resistivity as tantalum and makes a more stable resistor material [49a]. Previously sputter-deposited tantalum films had been electrolytically anodized to form a dielectric oxide, and with a sputter-deposited tantalum counter-electrode a thin film capacitor had been formed [49b].

In the late 1930s the "crossed field" (electric and magnetic) electron trap was used to enhance plasmas in sputtering from cylindrical-hollow (inverted) magnetrons (Penning 1936) [50], and cylindrical-post magnetrons by Penning and Mobius in 1940 [51] in some pioneering work on sputtering. In the "Penning discharge" a combination of electric and magnetic fields is used to confine the plasma near the surface of the sputtering target. By having an appropriate magnetic-field configuration, the electrons are trapped near the surface, giving increased ionization and a short distance for the positive ions to be accelerated to the target. This allowed sputtering to be performed at lower pressures and lower voltages, and at higher rates than with non-magnetic DC sputtering. In the post- and hollow-cylinder sources, the magnetic field is parallel to the surface, and the electrons are reflected by "wings" or flanges on the ends. For example, a simple post becomes a "spool" shape. Figure 8 shows some of Penning's patent figures. Various forms of the Penning magnetrons have been developed since that time. Notable are the works of Penfold and Thornton on post cathode magnetron sputtering in the 1970s [52] and Mattox, Cuthrell, Peeples, and Dreike in the late 1980s [53]. Heisig, Goedicke, and Schiller [54] and Glocker [55] improved on the inverted magnetron configuration.

In 1962 Anderson, Mayer, and Wehner reported on the RF sputtering of a film that had been deposited on the inside of a glass window [56]. This cleaning technique was based on a suggestion by Wehner in 1955 [57] and the earlier observations of Robertson and Clapp on the sputtering of the inside of a glass tube when a high-frequency gas discharge was produced [58]. Davidse and Maissel pursued RF sputtering to produce films of dielectric material sputtered from a dielectric target in 1966 [59]. In 1968 Hohenstein used co-sputtering of a glass with RF, and metals (Al, Cu, Ni) with DC, to form cermet resistor films [60]. One aspect of the effectiveness of RF sputtering (>1 MHz) is due to the self-bias that is generated on the surface of the insulator [61]. RF sputter deposition did not have a major impact on PVD processing for several reasons. These included the expense of large RF power supplies, and the problems associ-

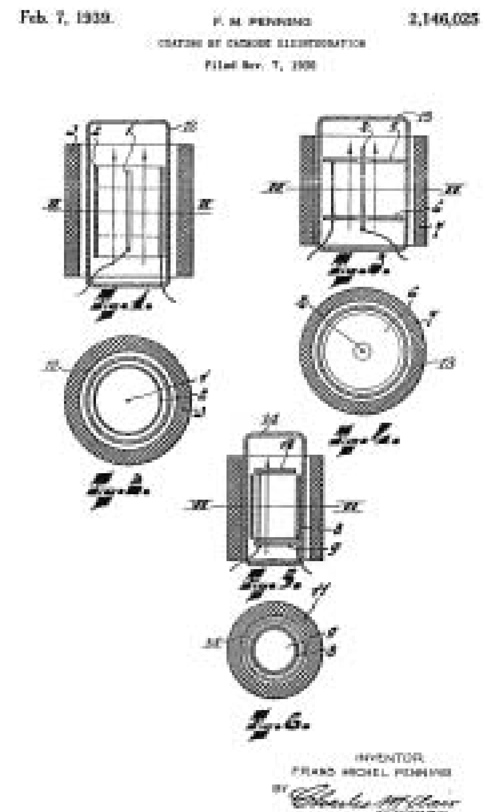

Figure 8. Penning magnetron configurations from his patent of 1939 [50].

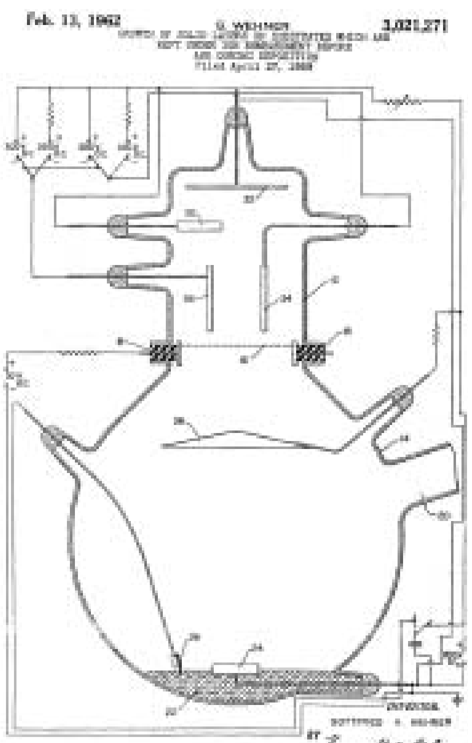

Figure 9. Wehner's Hg sputtering apparatus. In the figure, (36) is the sputtering cathode, (34) is the substrate, (22) is a mercury pool cathode, (16) is a graphite grid, (28) and (30) are anodes, and (32) is an "electron repeller" (1959) [62].

ated with introducing high thermal inputs (i.e., high sputtering rates) into insulator materials, which are generally very brittle and poor thermal conductors, without cracking them. The one material that was widely RF sputtered was SiO_2, which has a low coefficient of thermal expansion (CTE). In 1967 Schick RF sputter-deposited a chromium coating on razor blades (Krona-Chrome™ razor) for corrosion protection.

In 1962 Wehner patented the process of deliberate concurrent bombardment "before and during" sputter deposition using a "bias sputter deposition" arrangement and mercury ions [62] to improve the epitaxial growth of silicon films on germanium substrates and to lower the "epitaxial temperature." Figure 9 shows the apparatus he used. Later this process became known as bias sputtering (bias sputter deposition) and is one form of "ion plating." Maissel and Schaible used bias sputter deposition to improve the purity of sputter-deposited chromium films [63]. Cooke, Covington, and Libsch used "getter" sputter deposition to improve the purity of sputter-deposited films [64]. In 1966 d'Heurle compared the use of bias sputter deposition, getter sputter deposition, and a combination of the two for preparing pure molybdenum films (65). He obtained 30, 10, and 7 microhm-cm for the resistivities obtained with the respective techniques.

The triode sputtering configuration uses auxiliary plasma generated in front of the sputtering cathode by a thermoelectron emitting cathode and a magnetically confined plasma [66]. This arrangement was studied as a way to increase the plasma density and thus the sputtering flux that can be attained [67]. This sputtering technique lost its appeal with the development of magnetron sputtering.

In addition to the use of a deliberate substrate bias to accelerate charged particles to the substrate, high-energy particle bombardment can result from a "self-bias" on the substrate or from high-energy reflected neutrals resulting from ions that are de-ionized and reflected from the sputtering cathode [68]. This bombardment can cause "back ssputtering" of some of the deposited material [69]. High-energy bombardment of the substrate can also be by negative ions (e.g., O^-) accelerated away from the sputtering cathode [70]. Bombardment during deposition can also result in gas incorporation into the sputter-deposited material [71]. In non-biased, non-magnetron, planar diode sputter deposition, substrates in the line-of-sight of the cathode can be bombarded by high-energy electrons accelerated away from the cathode [72]. The substrates can be positioned in an "off-axis" geometry to avoid bombardment by positive ions, high-energy neutrals, or electrons [70].

In the early studies it was thought that the bombardment increased the purity of the sputter-deposited material and this was the reason that the deposited material had property values closer to those of the bulk (wrought) material [73]. It was not immediately recognized that the bombardment was causing densification of the deposited material; however, it was recognized that the bombardment affected crystallographic orientation [64, 74] and lowered the "epitaxial temperature" [62]. Bombardment was also shown to affect the film stress [75].

The effects of magnetic field on the trajectories of electrons had been realized even before Penning's work, and studies continued after Penning published his work on magnetrons [76]. The early Penning discharges used magnetic fields that were parallel to the sputtering target surface. Magnetron sources that use magnetic fields that emerge and reenter a surface ("magnetic tunnels") have a closed-loop electron path, and were used for sputtering were developed in the 1960s. These sources

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confine the electrons (and plasma) in a closed continuous "racetrack" on the target surface that does not cover the entire cathode surface. In 1962 Knauer patented an emerging and reentering closed-loop magnetic "tunnel" to trap electrons near the surface on both a post and a flat "washer-like" cathode electrode in a sputter-ion pump [77]. In 1963 Knauer and Stack described a closed magnetic tunnel on a post-cathode sputtering source for depositing films [78].

In 1968 Clarke developed a source using a magnetic tunnel on the inside of a cylindrical surface. This source became known as the "sputter gun" or "S-gun" [79] and is shown in Figure 10a. Mullaly at the Dow Chemical Co., Rocky Flats Plant (F-5) designed a magnetron source using a hemispherical target in 1969 [80]. Figure 10b shows the configuration of his magnetron sputtering source. Various magnetron configurations, including the planar magnetron, were patented by Corbani (patent filed July 1973, granted August 1975) [81]. Figure 10c shows figure 33 of Corbani's patent depicting a planar magnetron configuration. Chapin also developed a planar magnetron source (patent filed January 1974, granted August 1979) [82] and is credited with being the inventor of the planar magnetron sputtering source (F-6). Figure 10d shows the magnetron configuration depicted in Chapin's patent.

Major advantages of these magnetron sputtering sources were that they could provide a long-lived, high-rate, large-area, low-temperature vaporization source that was capable of operating at a lower gas pressure and higher sputtering rates than non-magnetic sputtering sources. With their new performance characteristics, sputtering sources began to replace thermal evaporation in some applications and enabled new applications to develop. In 1975 sputter-deposited chromium was used on plastic auto grills (Chevrolet). In the late 1970s planar magnetron sputter deposition was applied to coating architectural glass. In 1977 Charoudi applied planar magnetrons to coating webs for window mirror applications under contract to the U.S. Department of Energy [83]. The first commercial wide-web sputter coating machine, made by Leybold, began operation at Southwall Corp. in 1980. In the mid-1970s reactively sputter-deposited hard coatings on tools began to be developed [84], and they became commercially available in the early 1980s.

One disadvantage of the early emerging/re-entry magnetic field magnetron sources was that the plasma was confined to a small volume near the surface of the sputtering target and thus was not available to provide "activation" of reactive gases near the substrate for reactive deposition processes nor ions for the bias sputtering process. This presented problems in the reactive deposition of compound films such as nitrides. However, this disadvantage could be overcome by the use of auxiliary plasma sources. These plasmas could be formed by providing RF as well as DC on the sputtering target or by having auxiliary plasma, often magnetically confined, near the substrate. The use of such auxiliary plasmas was cumbersome, and their use decreased with the advent of the concept of the deliberate "unbalanced" (UB) magnetron source by Windows and Savvides in 1986 [85]. The unbalanced magnetron allows some electrons to escape from the confining EXB field and create plasma in regions away from the target surface. If the escaping magnetic field is linked to other UB magnetron sources (N to S poles), the plasma-generation region can be significantly increased [86]. This technique is widely used today. In a 1972 patent Davidse, Logan, and Maddocks used

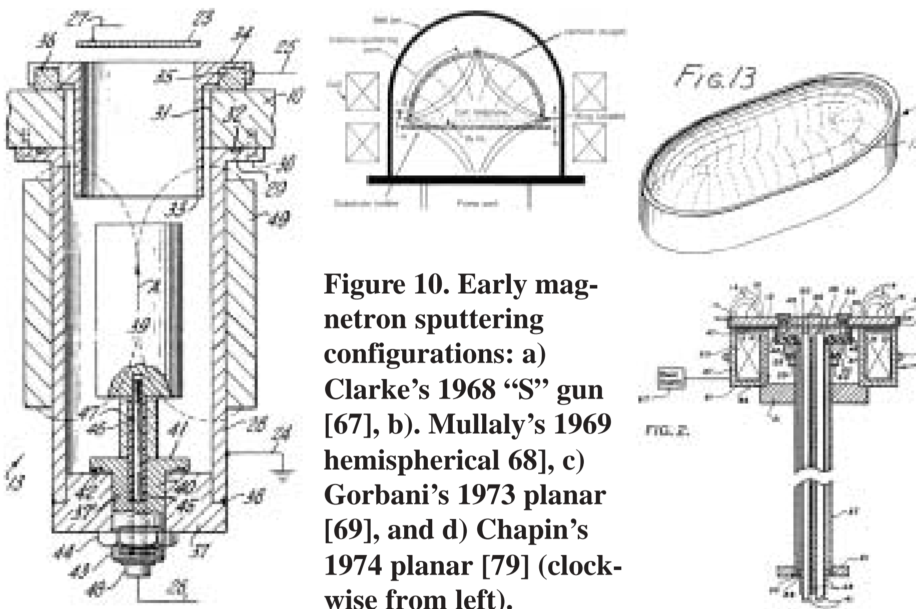

Figure 10. Early magnetron sputtering configurations: a) Clarke's 1968 "S" gun [67], b). Mullaly's 1969 hemispherical 68], c) Gorbani's 1973 planar [69], and d) Chapin's 1974 planar [79] (clockwise from left).

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magnets above the substrate fixture to draw electrons to the substrate and create a "self-bias" on the substrate using a non-magnetron sputtering cathode [87].

The DC planar sputtering configuration became the most popular magnetron design. A disadvantage of the planar magnetron is that the "racetrack" erosion path gives non-uniform erosion over the target surface, low target-material utilization, and a non-uniform deposition pattern. In order to obtain uniform deposition on a substrate it is typically necessary to fixture and move the substrate in a specific manner or to have a moving magnetic field in the target. Another disadvantage is in reactive sputter deposition of highly insulating materials where the planar magnetron sources can be "poisoned" by the formation of a compound on the surface in areas outside the racetrack. This can cause surface charge buildup and arcing (flashover). To avoid this problem, RF can be superimposed on the DC target power, as was done by Vratny in 1967 on non-magnetron reactive sputter deposition [88], or "pulsed power" can be applied to the target. In 1977 Cormia patented the use of symmetrical or asymmetrical AC power on a single-cathode magnetron at a frequency of 400 Hz to 60 kHz ("mid-frequency") to create "pulsed power" on the cathode [89]. In this arrangement the target has a positive polarity during a portion of the wave cycle to allow electrons from the plasma to neutralize positive charge buildup on the poisoned surface.

Other target arrangement can be used to provide uniform erosion over the target surface. An example is to move the magnetic field behind the target. A variation on moving the magnetic field is to move the sputtering surface through the magnetic field by designing an elongated racetrack magnetic field formed by magnets inside a hollow cylinder that is rotated, which moves the surface through the field. This rotatable cylindrical magnetron was patent by McKelvey in 1982 [90]. The patent was assigned to Shatterproof Glass, but Airco bought the patent when Shatterproof Glass went bankrupt [91]. Major advantages to this design are the good utilization of the sputtering target material and the removal of most of the "poisoned" areas on the target as it rotates. This sputtering target design is in common use today (e.g., BOC's C-Mag™).

In 1987 Quazi patented sputtering from a single magnetron sputtering target using discrete pulses of bipolar (alternately positive and negative) pulsed power that allowed the sputtering target to discharge any positive-charge buildup on the target (dielectric or "poisoned" metal surface) during the positive portion of the waveform [92]. Figure 11 shows the waveform and system configuration from his patent. This technique is similar to the "counterpulse" used to extinguish arcs in vacuum arc switch technology [93]. This concept was an improvement over the asymmetrical AC power used previously because the waveform could consist of square waves with fast rise and decay times and the pulse lengths could be varied independently. In 1993 Frach, Heisig, Gottfried, and Walde utilized the single-cathode bipolar pulsed power concept to reactively deposit dielectric films using a "hidden anode" to minimize the "disappearing anode" effect [94].

In 1988 Este and Westwood reported the mid-frequency dual-magnetron sputtering arrangement where the two targets were alternately cathodes and anodes [95]. This arrangement prevented the "disappearing anode" effect when reactively depositing highly insulating dielectric films and also prevented charge buildup and arcing (flashover) on the targets. Independently investigators at Kodak Research Laboratories were working on the same dual-cathode design and they used the technique to reactively sputter-deposit insulating films on web material in a roll coater in mid-1989 [96]. Scherer, Schmitt, Latz, and Schanz commercialized the

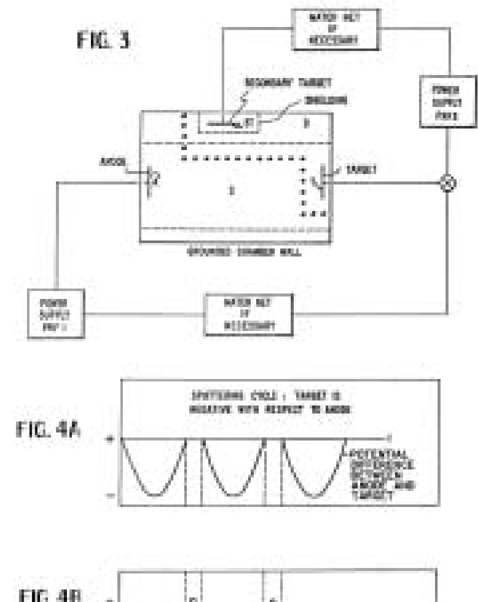

Figure 11. Circuit (a) and bi-polar waveform on the target cathode (b) of Quazi's dual-cathode (one is "hidden") pulsed magnetron sputtering system (1986) [92].

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dual planar magnetron configuration in 1992, as shown in Figure 12 [97], and it is in wide use today (e.g., Applied Films' TwinMag™). In 2000 Glocker, Lindberg, and Woodard reported using dual inverted cylindrical magnetrons in a similar manner to dual-planar magnetrons [98]. In the early 1990s several companies began making high-power, mid-frequency, bipolar pulsed power supplies. Pulsed sputtering has been found to improve the properties of many films. This may be attributed to periodically higher plasma potentials caused by the pulsing and thus higher sheath potentials or it may be due to the high "spike" voltages during ignition, creating pulses of high-energy reflected neutrals that bombard the growing film.

There are many other variations on magnetron sputtering, including a target where the racetrack can either be a sputtering area or a steered arc track [99]. This system is used for the ArcBond™ process (Hauzer Techno Coatings) where the initial layer is deposited by arc vapor deposition, and the coating is built up by sputtering. This is done to minimize the number of molten particles ("macros") formed during arc vapor deposition that create defects in the coating. In 1999 a magnetron system using one magnetron and two non-magnetron electrodes that were alternately at positive and negative potentials was introduced and called the "dual-anode magnetron," even though there was only one anode (and two cathodes) at a time present in the circuit [100]. The magnetron sputtering cathode is always negative with respect to the active anode and the polarity on the magnetron passes through zero

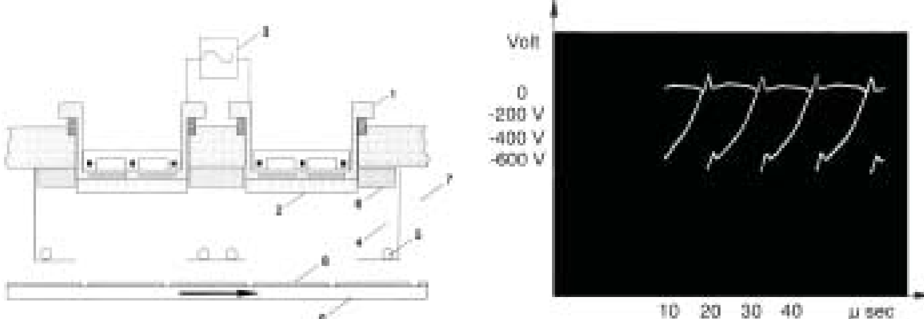

Figure 12. Scherer et al: a) dual planar cathode arrangement for coating flat glass; b) Voltage waveform on a cathode (1992) [97].

twice on each voltage cycle, thus allowing charge buildup on the magnetron target to be neutralized. Anodes 1 and 2 are alternately positive (anodic) and negative with twice the negative voltage that appears on the magnetron. This allows the electrodes that act as anodes to be sputter cleaned on each cycle, thus avoiding the "disappearing anode" effect.

"Directed deposition" is confining the vapor flux to one axis by eliminating off-axis components of the flux. Directed deposition can be attained by collimation of the vaporized material. In sputtering this can be done using a "honeycomb" structure between the source and the substrate [101]. Another type of directed sputter deposition is the use of a gas flow to direct the sputtered material from the interior of a hollow cathode to the substrate [102]. This has been termed "gas flow sputtering" (GFS).

Generally very little sputtered material is ionized before it is deposited. Some techniques increase the ionization of the atoms by postvaporization ionization using plasmas and magnetic fields to form "film ions" that can be accelerated to the substrate surface when it has a negative bias (i-PVD) [103]. This encourages the depositing material to impinge on the substrate normal to the surface and increase the filling of high-aspect-ratio surface features. This is another type of "directed deposition" process.

Some work has been done using post-ionized sputtered species ("self-ions") to form the plasma used for sputtering ("self-sputtering"). Both a molten (thermal evaporating) cathode [104] and a solid magnetron target [105] with no gaseous species present have been used.

The technique of ion beam sputtering (and ion beam sputter deposition) was first used in the late 1960s [106]. Ion beam sources were developed from the ion propulsion engines developed by NASA in the 1950s [25]. There are two types of ion sources—an ion "gun" that has a defined ion energy and low beam dispersion, and a "broad-beam" that has a large dispersion and a spectrum of energies [107]. Two ion beams may be used—one to sputter the material and the other to bombard the depositing material. The use of ion beams to bombard the depositing material is called Ion Beam Assisted Deposition (IBAD). In this process, which will be discussed under ion plating, the ion beam provides the

bombardment of the depositing material from any vaporization source. The bombarding ions can either be an inert species or a reactive gas [108]. Ion beam sputter deposition is not widely used; however, ion beam "milling" (etching) to form surface features or ion beam "polishing" to smooth surfaces are used in some cases. One of the first significant commercial uses of ion beam reactive sputter deposition was the coating of ring laser gyro (RLG) mirrors [109]. The RLG has no moving parts and relies on extremely high-quality multilayer coated mirrors.

The Scanning Electron Microscope (SEM) was first available in 1965 from Cambridge Scientific Instruments. The SEM provided an analytical tool that allowed studies on the growth morphology of sputter-deposited materials and the effects of concurrent bombardment on the growth [110]. In 1977 Thornton published a "Structure-Zone Model," patterned after the M-D diagram for evaporation-deposited coatings [111], which came to be known as the "Thornton Diagram" [112]. The Thornton Diagram illustrates the relationship between the deposit morphology, the deposition temperature, and the pressure in the sputtering chamber. Of course the sputtering pressure determines the flux and energy of the reflected high-energy neutrals from the sputtering cathode, so the diagram reflects the degree that the depositing material is bombarded by energetic particles during deposition. In 1984 Messier, Giri, and Roy further refined the Structure Zone Model [113].

The columnar growth found in thick vacuum deposits is dependent upon the angle-of-incidence of the depositing flux, the surface roughness, the deposition temperature, and the amount of concurrent energetic particle bombardment [114]. By using a low angle-of-incidence and varying the angle-of-incidence (GLAD—glancing angle deposition), "sculpted films" can be grown [115].

Also in the 1970s there were a number of studies on the effect of processing variables, particularly concurrent bombardment, on the intrinsic stress of sputter-deposited films [116]. In 1988 periodic variation of pressure ("pressure cycling") was used by Mattox, Cuthrell, Peeples, and Dreike to control the total stress in thick sputter-deposited layers of molybdenum by depositing alternate layers having compressive and tensile stress. This was accomplished by periodically changing the gas pressure, and thus the flux and energy of bombardment by reflected high-energy neutrals [117].

In 1984 Sproul and Tomashsk patented a mass spectrometric-feedback method of controlling the partial pressure of reactive gases in reactive sputter deposition [118]. Optical emission spectroscopy (OES) is also used to control the partial pressures of reactive gases in reactive sputter deposition [119]. OES developed from the "end-point" detection used in plasma etching [110].

With the advent of magnetron sputtering, controlled reactive sputter deposition, and the use of controlled concurrent ion bombardment as a process parameter, sputter deposition rapidly developed after the mid-1970s. Applications of sputter deposition have rapidly increased since that time. Today applications of sputter deposition range in use from depositing semiconductor device metallization, to coating architectural window glass for energy conservation, to coating tool bits, to coating plumbing fixtures for decorative purposes, to coating web material with transparent vapor barriers for packaging. In some cases sputter deposition has replaced electroplating or has displaced thermal evaporation PVD, but generally it has generated new applications and markets.

The term "sputtering" is probably an outgrowth of the controversy over whether this type of vaporization was thermal evaporation ("electrical evaporation") [39] or whether it was due to a non-thermal (momentum transfer) process [121]. Initially the English term "spluttering" (F-6a) was used, which became sputtering several years later. To quote G.K. Wehner [122]:

"Sometimes the question is raised as to who introduced the word 'sputtering.' A literature search shows that Sir J.J. Thompson [170] used the word 'spluttering' but that I. Langmuir and K.H. Kingdon eliminated the 'l' in their publications in the years 1920 to 1923. In 1923, the Research Staff of the General Electric Co., London [171] still used only the term 'cathode disintegration.' Kay [172] following a suggestion by Guentherschulze [173], tried without much success to introduce the term 'impact evaporation.'"

Unfortunately Wehner has the wrong date (1921) in his reference to Sir J.J. Thompson's book. The correct date for that publication is 1913.

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The manner in which Thompson used the term spluttering (e.g., "A well-known instance of this is the 'spluttering' of the cathode in a vacuum tube; —") [123] would seem to indicate that this was still not the first use of the term.

By 1930 the term "sputtering" was being used for the deposition process (e.g., "sputtered films") as well as the vaporization process. This at times leads to confusion. A more proper term for the deposition process would be "deposition by sputtering" or "sputter deposition."

Thermal Evaporation [2, 124-127]

Thermal evaporation is the vaporization of a material by heating to a temperature such that the vapor pressure becomes appreciable and atoms or molecules are lost from the surface in a vacuum. Vaporization may be from a liquid surface (i.e., above the melting point) or from a solid surface (i.e., sublimes). The author has arbitrarily defined 10^{-2} Torr as the equilibrium vapor pressure above which the free-surface vaporization in PVD-type vacuums is enough to allow vacuum deposition to occur at a reasonable rate [127]. If the material is solid at that temperature the material is said to sublime (e.g., Cr, Mg) and, if molten, is said to evaporate (e.g., Al, Pb, Sn, Mo, W). A few materials have a vapor pressure such that they can either be sublimed or evaporated at temperatures near their melting point (e.g., Ti). Some compound materials sublime and some evaporate.

Thermal evaporation studies in vacuum began in the late 1800s with the work of H. Hertz [128] and S. Stefan [129], who determined equilibrium vapor pressures—but they did not use the vapor to form films. Knudsen proposed "Knudsen's Cosine Law of Distribution" for vapor from a point source in 1909. In 1915 Knudsen refined the free-surface vaporization rate as a function of equilibrium vapor pressures and ambient pressure [130], and the resulting equation is known as the Hertz-Knudsen equation for free-surface vaporization. Honig summarized the equilibrium vapor pressure data in 1957 [131].

Thermal evaporation by "heating to incandescence" and film deposition was covered by Edison's 1894 patent (applied for in 1884) [35]. Edison did not mention evaporation from a molten material in his patent and many materials will not vaporize at an appreciable rate until they are at or above their melting temperature. Edison did not use the process in any application, presumably because radiant heating from the source was detrimental to the vacuum materials available at that time. In 1887 Nahrwold reported the formation of films of platinum by sublimation in vacuum [132], and he is sometimes credited with the first use of thermal vaporization to form films in a vacuum. In 1907 Soddy proposed the vaporization of calcium onto a surface as a method of reducing the residual pressure in a sealed tube ("gettering") [133]. This would have been the first "reactive deposition" process.

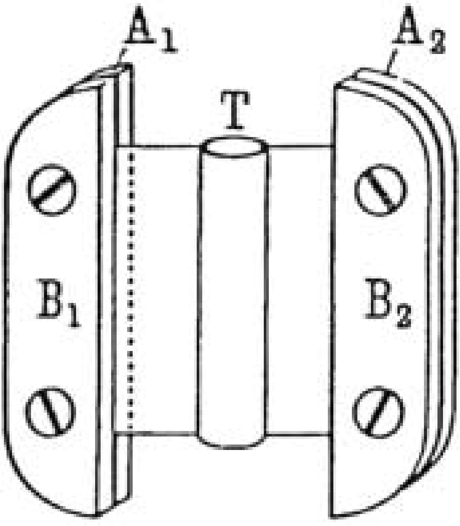

Figure 13. von Pohl and Pringsheim crucible evaporation source using a heated foil held in clamps (1912) [134].

In 1912 von Pohl and Pringsheim reported forming films by the evaporating materials in a vacuum from a magnesia crucible that was heated by a resistively-heated foil surrounding the crucible, as shown in Figure 13 [134].. They are sometimes credited with the first deposition by thermal evaporation in vacuum. Langmuir studied the vaporization rate of materials in vacuum in 1913 [135] and reported forming films. In 1931 Ritschl reported thermal evaporation of silver from a tungsten wire basket to form half-silvered mirrors [136]. Ritschl is often credited with being the first to use evaporation from filament to form a film in vacuum. Cartwright and Strong reported evaporating metals from a tungsten wire basket in 1931 [137], but the technique was not successful for evaporating aluminum because molten aluminum wets and alloys with the tungsten wire, which causes it to "burn out" when there is a relatively large volume of molten aluminum. Aluminum was success-

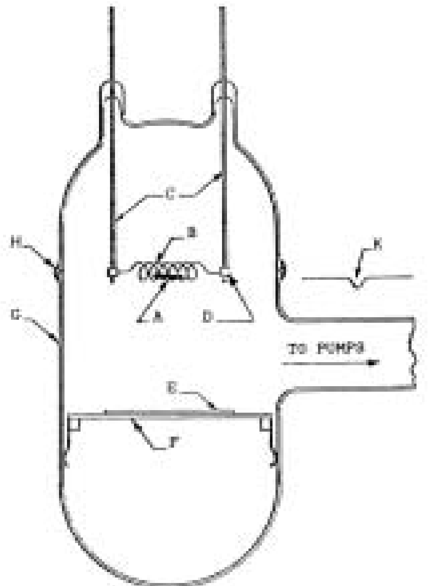

Figure 14. Glass vacuum chamber used for filament thermal evaporation. The chamber could be "cracked" (at h) and reused using sealing wax (1931) [46].

fully evaporated by Strong in 1935 from heavy-gauge tungsten wire that was wetted by the molten aluminum [138].

In 1931 the Bureau of Standards in their circular on making mirrors [46] discussed the "common" technique of sputtering and the "the deposition of metals by evaporation." In the description the Bureau stated, "This method of deposition has not been widely tested, and its possibilities are therefore little known, but it would seem to be especially valuable for small work where films of any readily volatile substance are required." Figure 14 (figure 4 in the circular) illustrates evaporation of material from an open wire coil in a glass chamber that has to be "cracked" in order to remove the deposited film. The chamber could be re-used by joining the sections with sealing wax. In the circular, W.W. Nicholas was named as the investigator at the Bureau of Standards and refers to other investigators (J. E. Henderson and A.H. Pfund) who were investigating thermal evaporation from filaments as a means of depositing films in vacuum. In that circular it was noted that J.E. Henderson was evaporating nickel that had been electroplated onto a tungsten wire to provide an "especially uniform deposit." Strong described the same technique in 1932 [139]. Edison, in his 1894 patent, discussed depositing (e.g., electroplating) a material on carbon, then heating the carbon to vaporize the material in vacuum [35].

J. Strong of Johns Hopkins University and later the California Institute of Technology (1947), where he worked on metallizing the 200" Palomar telescope, did a great deal of development using thermal evaporation of aluminum from multiple tungsten filaments for coating astronomical mirrors [140] (F-9). Strong, with the help of designer Bruce Rule, aluminum coated the 200" Palomar ("Hale") astronomical telescope mirror in 1947 (the telescope mirror was started before WWII) [141] using multiple (350) filaments and a 19' diameter vacuum chamber [142]. In 1937 D. Wright of GE began development of the sealed-beam headlight, which first appeared on autos in 1940 [143] (F-10).

In 1817 Fraunhoffer noted that optical lenses improved with age due to the formation of a surface film. Following this discovery many investigators artificially aged lenses to form antireflection (AR) coatings. For example, in 1904 H.D. Taylor patented (British) an acid treatment of a glass surface in order to lower the index of refraction and the reflectivity by producing a porous surface. In 1933 A.H. Pfund vacuum-deposited the first single-layer (AR) coating (ZnS) while reporting on making beam-splitters [144] and Bauer mentioned AR coatings in his work on the properties of alkali halides [145]. In 1935, based on Bauer's observation, A. Smakula of the Zeiss Company developed and patented AR coatings on camera lenses [145a]. The patent was immediately classified as a military secret and not revealed until 1940 (F-10a). In 1936 Strong reported depositing AR coatings on glass [146]. In 1939 Cartwright and Turner deposited the first two-layer AR coatings [147]. One of the first major uses of coated lenses was on the projection lenses for the movie *Gone With the Wind,* which opened in 1939 (S. Peterson of Bausch & Lomb Optical Co.) [148]. The AR coated lenses gained importance in WWII for their light-gathering ability in such instruments as rangefinders and the Norden Bombsight [149]. During WWII baking of MgF_2 films to increase their durability was developed by D.A. Lyon of the U.S. Naval Gun Factory [150]. The baking step required that the lens makers coat the lens elements prior to assembly into compound lenses. In 1943 (Oct.) the U.S. Army (The Optical Instrument Committee, Frankfort Arsenal) sponsored a conference on "Application of Metallic Fluoride Reflection Reducing Films to Optical Elements." The conference had about 132 attendees. The proceedings of this conference (112 pages) is probably the first extensive publication on coating optical

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elements [151]. O.S. Heavens published his classic work, *Optical Properties of Thin Solid Films* (Butterworth Scientific Publications), in 1955.

The Germans deposited CaF_2 and MgF_2 AR coatings during WWII [152]. Plasma cleaning of glass surfaces is reported to have first been used by Bauer at the Zeiss Company in 1934 [152]. The Schott Company (Germany) was also reported to have deposited three-layer AR coatings by flame-pyrolysis CVD during WWII [152].

Vacuum evaporation of metals (Cd and Zn) on paper web for paper-foil capacitors was begun in about 1935 by R. Bosch of the Bosch Company of Germany, who discovered that there was a “self-healing” effect when there was an arc between the low-melting-point thin film electrode materials [153]. By 1937 the Germans had demonstrated that the use of a “nucleating layer” increased the adhesion of zinc to a paper surface [154]. The effect of a nucleating layer on film formation had been noted by Langmuir as early as 1917 [155]. Vacuum evaporation of metals onto paper was used to produce radar chaff by Whiley in Britain during WWII. In 1958 the U.S. military formally approved the use of “vacuum cadmium plating” for application as corrosion protection on high-strength steel to avoid the hydrogen embrittlement associated with electroplated cadmium [156]. In recent years PVD processing has been used to replace electroplating in a number of applications to avoid the water pollution associated with electroplating.

In 1907 von Pirani patented the vacuum melting of refractory materials using focused cathode rays (electrons) from a glow discharge [157]. (W. Crookes noted that he could fuse the platinum anode in his gas discharge tubes in 1879.) In his patent von Pirani did not mention film formation, but he may have deposited films during the vacuum melting operation at low gas pressures. Figure 15 shows the figure from his patent that illustrates focused electron beam melting. In 1933 H.M. O’Brian and H.W.B. Skinner utilized accelerated electrons to heat a graphite crucible and evaporate materials [158]. Subsequently a number of non-focused (“work accelerated”) electron bombardment evaporation source designs were developed. In 1951 Holland patented the use of accelerated electrons to melt and evaporate the tip of a wire (“pendant drop”), which involved no filament or crucible [159]. In 1949 Pierce described the “long-focus” electron beam gun for melting and evaporation in vacuum [160]. The long-focus gun suffers from shorting due to the deposition of evaporated material on the filament insulators that are in line-of-sight of the evaporating material. Deposition rates as high as 50 µm/s have been reported using e-beam evaporation (161).

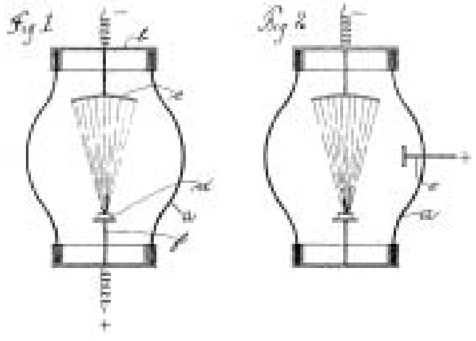

Figure 15. Vacuum melting using focused “cathode rays” (Pirani 1907) [157].

To avoid exposure of the filament to the vapor flux, bent-beam electron evaporators were developed [162]. In 1968 Hanks filed a patent on a 270° bent-beam electron beam evaporation source [163] that has become the most widely used. Rastering the electron beam allows the energy of the electron beam to be distributed over the surface. In 1978 H.R. Smith described a unique horizontally emitting electron beam (EB) vapor source [164]. The source used a rotating crucible to retain the molten material, and its function was to coat large vertical glass plates. As early as 1970 Kurz was using an electron-beam system to evaporate gold for web coating [47]. In electron beam evaporation a high negative “self-bias” can be generated on the surface of an insulating material or on an electrically isolated fixture. This bias can result in high-energy ion bombardment of the self-biased surface [165].

A number of thermoelectron-emitter e-beam source designs followed, including rod-fed sources and “multi-pocket” sources. The high voltage on the filament prevented the source from being used in a plasma where ions accelerated to the cathodic filament; this caused rapid sputter-erosion of the filament. In 1971 Chambers and Carmichael [166] avoided that problem by having the beam pass through a small hole in a thin sheet in a section of a plate that separated the deposition chamber from the chamber where the filament was located. This allowed a plasma to be formed in the deposition chamber while the filament chamber was kept under a good vacuum. The plasma in the deposition chamber

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allowed ion bombardment of the depositing film material as well as "activation" of reactive gas.

The use of a hollow cathode electron emitter for e-beam evaporation was reported by J.R. Morley and H. Smith in 1972 [167]. In 1951 Picard and Joy described the use of evaporation of materials from an RF-heated crucible [168]. In 1966 Ames, Kaplan, and Roland reported the development of an electrically conductive TiB_2/BN composite ceramic (Union Carbide Co., UCAR™) crucible material that was compatible with molten aluminum [169].

Directed deposition is confining the vapor flux to one axis by eliminating off-axis components of the flux. Directed deposition can be attained by collimation of the vaporized material. In evaporation this was done by Hibi (1952) who positioned a tube between the source and the substrate [170]. Collimation was also attained by H. Fuchs and H. Gleiter in their studies of the effects of atom velocity on film formation using a rotating, spiral-groove, velocity selector [171]. In 1983 Ney described a source that emitted a gold atom beam with a 2° divergence [172]. Recently "directed deposition" has been obtained using a flux of thermal evaporated material projected into a directed gas flow [173].

When thermally evaporating alloys, the material is vaporized with a composition in accordance to Raoult's Law (1887) [174]. This means that the deposited film will have a continuously varying composition unless very strict conditions are met as to the volume of the molten pool using a replenishing source [175]. One way of avoiding the problem is by "flash evaporation" of small volumes of material. In 1948 L. Harris and B.M. Siegel reported flash evaporation by dropping small amounts of material on a very hot surface so that all of the material was vaporized before the next material arrived on the hot surface [176]. In 1964 Smith and Hunt described a method for depositing continuous strips of alloy foils by evaporation [177]. Other free-standing thin film structures are also deposited, such as beryllium X-ray windows and nuclear targets [178].

Evaporation or sublimation of compounds can result in extensive molecular disassociation. Some compound materials can be vaporized without significant disassociation. These include many halides, sulfides, and selenides, as well as a few oxides (such as SiO). Many of these compound materials were used in early optical coating "stacks," and for many years thermal evaporation was almost the only PVD technique for depositing optical coatings. During sublimation of these materials, some of the material comes off as "clusters" or chunks. "Baffle" or "optically dense" sources were developed that required vaporization from several hot surfaces or deflection of the particles before the vapor could leave the source [179]. This generated a more uniform molecular vapor. Baffle sources can also be used to evaporate material in a downward direction. Sublimed SiO coatings were used on mirrors for abrasion resistance by Heraeus (Germany) before WWII [180]. Following the deposition they were heated in air to increase oxidation. In 1950 G. Hass evaporated lower-oxide materials in an oxygen atmosphere in order to increase the state of oxidation [181].

In 1952 Aüwarter patented the evaporation of metals in a reactive gas to form films of compound materials [181]. In 1960 Aüwarter proposed that evaporation of a material through a plasma containing a reactive species be used to form a film of compound material [182]. Many investigators studied these methods of depositing transparent optical coatings. In 1964 Cox, G. Hass, and Ramsey reported their use of "reactive evaporation" for coating surfaces on satellites [183]. In 1972 R.F. Bunshah introduced the term "activated reactive evaporation" (ARE) for evaporation into a reactive plasma to form a coating of a compound material [184].

"Gas evaporation" is a term used for evaporation of material in a high enough gas pressure such that there is multi-body collisions and gas phase nucleation. This results in the formation of fine particles that are then deposited [185]. A.H. Pfund studied the optical properties of fine particles in 1933 [186]. It is interesting to note that during gas evaporation performed in a plasma, particles become negatively charged and remain suspended in the plasma—since all the surfaces in contact with the plasma are negative with respect to the plasma. Electrically charged gas-phase-nucleated particles can be accelerated to high kinetic energies in an electric field. This is the basis for the "ionized cluster beam" (ICB deposition process introduced by Takagi et al in 1974 that used a thermal-evaporation, nozzle-expansion type source [187] (F-11). Gas phase

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nucleation (gas-condensation) has also been used to form neutral and ionized ultrafine particles (nanoparticles) using a sputtering source and a plasma condensation chamber (188).

In 1965 Smith and Turner described the use of a ruby laser to vaporize (flash evaporate) material from a surface and deposit a film [189]. This process is sometimes called laser ablation and the deposition process, laser ablation deposition (LAD) [190]. LAD and reactive-LAD have found application in the deposition of complex materials such as superconductive [191] and ferroelectric thin films.

Molecular beam epitaxy (MBE) is an advanced, sophisticated vacuum deposition process used to deposit single-crystal films on single-crystal substrates (epitaxy or “oriented overgrowth”). Epitaxy has been known since the 1920s and was reviewed by Pashley in 1956 [192]. The modern use of MBE in semiconductor device fabrication began with Cho and Arthur in 1975 with the growth of III-V semiconductor materials [193].

Before the end of WWII, the thickness of deposited optical coatings was determined by visually observing the transmittance or reflectance during deposition. Around 1945 optical instrumentation was developed for monitoring the thickness during deposition [194]. In 1959 Steckelmacher, Parisot, Holland, and Putner described a practical optical monitor for use in controlling the film thicknesses in multilayer interference coatings [195]. In the late 1950s quartz crystal monitors (QCMs) began to be developed for determining the mass of deposited material *in situ* [196]. After WWII the development of laser technology, particularly high-energy lasers, required very high quality optical and reflecting coatings [197].

Arc Vapor Deposition [13, 198-200]

Discussion of arcs and arc vapor deposition is somewhat difficult due to the varying definitions of an arc. These definitions vary from “a low-voltage, high-current discharge between electrodes,” to “a discharge in a gas or vapor that has a voltage drop at the cathode of the order of the minimum ionizing or minimum exciting potential of the gas or vapor” (K.T. Compton) [198], to “a self-sustained discharge capable of supporting large currents by providing its own mechanism of electron emission from the negative electrode” (J.M. Lafferty) [13]. The history of the study of arcs, sparks (low total-power arcs), and “flashovers” (short-duration arcs and sparks over the surface of an insulator) is quite old, with studies of the chemistry in spark plasmas predating the invention of the voltaic battery. With the invention of the voltaic battery (Volta, 1800), high-current, low-voltage electric power was available and the study of chemistry in arcs ensued [21]. In 1839 Dr. Robert Hare described the first arc furnace that was used for melting materials in controlled atmospheres [201], and in 1903 Dr. von Bolten used an arc in vacuum to melt materials [201].

Michael Faraday may be credited with vacuum depositing the first material that was studied for its properties (optical) in 1857 [202]. The film was probably deposited by arc vaporization (“spark between two points of wire”), though some authors have called it an exploding wire. The work was a minor part of Faraday’s studies on the optical properties of fine particles (“colloidal”) of gold, mostly prepared from chemical solutions. The technique was not pursued but was referred to by A.W. Wright in his 1877 paper on “electrical deposition” [32].

In non-self-sustaining arcs, the electron emission from the cathode may be from thermal heating (thermoelectron emission) [203] or from a hollow cathode [204]. In arc vapor deposition for PVD, vaporization can either be from a molten (usually) anode (“anodic arc”) or from a molten spot on a solid (usually) cathode (“cathodic arc”). An advantage of both types of arcs is the high percentage of ionization of the material vaporized from the electrodes, as well as gases that may be present. The ions of the vaporized material (“film-ions” or “self-ions”) may be accelerated to high kinetic energies. This notable property is the primary reason that the author has treated arc vapor deposition separately from thermal evaporation.

In 1884 Edison filed a patent entitled “Art of Plating One Material on Another” that included arc vaporization as a deposition technique [35]. Figure 16 shows the figure from his patent that was related to arc vaporization. This aspect of the patent was challenged based on Wright’s work, as was discussed previously. Edison was finally granted the patent

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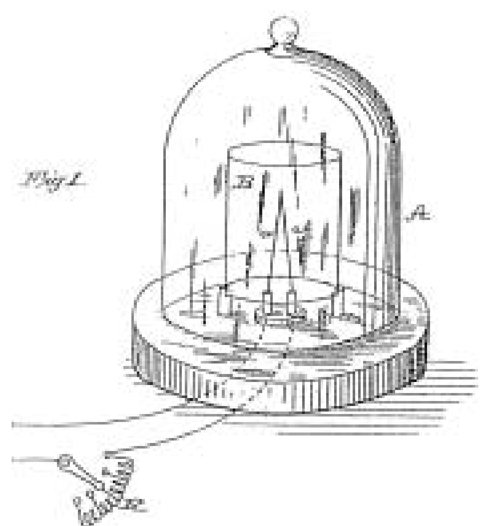

Figure 16. Edison's arc vapor deposition apparatus as shown in his 1894 (filed 1884) patent [35].

in 1894 after modifying his claim to call his arc a "continuous arc" and that of Wright a "pulsed arc" and a "laboratory curiosity." Edison attempted to use arc vaporization to deposit the "seed" layers on his wax phonograph masters. In a 1902 patent entitled "Process of Coating Phonograph-Records," he stated, "I find that in practice that the employment of an electric arc for vaporizing the metal, as suggested in my patent, to be open to the objection of being slow, and unless the process is carried on with great care the deposit is not entirely uniform, while there is danger of injuring the very delicate phonographic-record surface, particularly from the heat of the arc." Instead, he used a configuration that was obviously sputtering, as shown in Figure 7 [37]. Several vacuum arc vapor sources (as well as others) were developed during WWII to form ion beams for use in the magnetic isotope separation program [205]. These ion beams formed vacuum deposits but they were not studied for their properties. Arc vapor deposition activities then died down until well after WWII.

In 1954 Bradley deposited carbon films using a pointed rod-type carbon arc vapor source [206]. In 1962 Lucas, Vail, Stewart, and Owens deposited refractory metal films [207] by arc vapor deposition. In 1965 Kikushi, Nagakura, Ohmura, and Oketani investigated the properties of a number of metal films deposited from a vacuum arc [208]. In 1965 Wolter investigated the properties of Ag, Cu, and Cr films deposited by "anodic" arc vapor deposition from a molten metal using a heated electron-emitting filament as the cathode [209]. In 1972 Morley and Smith used a hollow cathode electron source for rapidly evaporating material for film deposition [167, 210]. Later Ehrich continued to develop the molten anodic arc deposition system [211].

In the "cathodic arc" discharge, vaporization originates from a spot on the surface. The spot may be stationary ("attached"), but it usually moves over the surface naturally or under the influence of a magnetic field. In the mid-1970s workers in the Soviet Union, while working on plasma sources, developed sources for arc vaporization and film deposition using arcs moving over a surface. Some of their work involved reactive deposition of nitrides (F-12). Some of the early patents on arc vaporization sources were by Snaper (1974—magnetic field coils) [212], Sablev et al (1974—no magnetic field) [213], and Mularie (1984) [214]. Figure 17 shows a figure from the Snaper patent. Generally arc deposition sources use DC though pulsed sources have been developed [215].

Early cathodic arc sources used "random" or "steered" arcs on planar surfaces. The arcs are initiated by a high-voltage "trigger arc" or by making and breaking electrical contact to the surface. Recently laser pulses have been used to trigger the arcs [216]. In 1991 Vergason patented a cathodic arc source where vaporization was from arcs that traveled from one end of a long rod to the other as the negative contact was changed from one end of the rod to the other, and a "trigger arc" initiated the main arc at the end opposite from the electrical contact. In traversing the length of the rod, the arcs give uniform erosion over the surface of the rod [217]. Figure 18 shows figures from that patent. In 1993 Welty added a low-turn, current-carrying coaxial coil around the rod to provide an additional axial magnetic field that aided in spiraling the arc around the cathode rod and controlled the arc travel time [218].

An advantage of arc vaporization is that a large fraction of the vaporized material is positively ionized [219] and these "film ions" can be accelerated to the substrate surface if there is a negative potential on the substrate (see ion plating section). In gaseous arcs the dissociation, ionization, and excitation of the

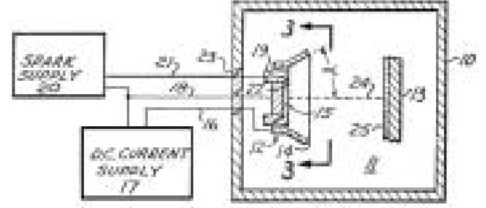

Figure 17. Cathodic arc vaporization source as shown in Snaper's patent (1974) [212].

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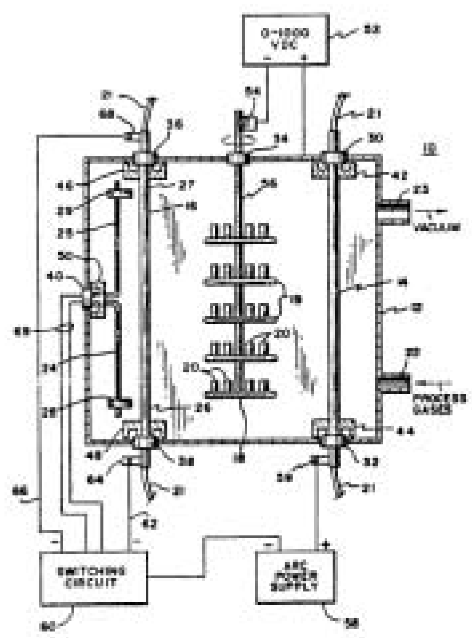

Figure 18. Figure from Vergason's patent showing a rod-type cathodic arc vaporization source (1990) [217].

reactive gas ("activation") can be important in reactive deposition processes.

A disadvantage of cathodic arc physical vapor deposition (CAPVD) is the generation of molten "macroparticles" during arcing. These "macros" create bumps and pinholes in the film. One method of eliminating the macros is to use a "filtered arc source" where the plasma of "film ions," gaseous ions, and electrons is deflected out of the line-of-sight of the source. Most of the macros and uncharged film atoms are deposited on the walls. This approach reduces the deposition rate on the substrate significantly. The most common design uses a quarter-torus plasma duct [220]. Beginning in the 1990s the Royal Australian Mint used filtered arc deposition to deposit TiN hard coatings on their coining dies [221].

Arc vapor sources can provide ions of the depositing material to sputter a target of the same material [222]. This technique eliminates the "macros." The use of a magnetic field arrangement to increase the electron path length in front of the arc cathode may be used to increase ionization and heat "macros" to increase the evaporation from the macros after they are ejected [223]. A modified tungsten-inert-gas (TIG) plasma arc welding source has been used to provide a plasma for melting and evaporating a material in vacuum [223a].

A magnetron source that used magnetic fields that emerge and re-enter a planar mercury surface ("magnetic tunnel," described in the sputter deposition section) was developed by Kesaev and Pashkova in 1959 for steering arcs [224]. Steered arc vaporization can be done with the same configuration as planar magnetron sputtering [225]. Sputtering and arc vaporization can be combined into the same target by changing the magnetic field configuration [99]. This allows arc vaporization to be used for depositing the "adhesion layer," then the film thickness is built up using sputtering where there are no macros (ArcBond™ process). Arc vaporization as a vapor source can be used with a continuous or pulsed bias [226] to extract ions from a plasma to bombard the growing film (ion plating).

The use of a capacitor discharge through a thin wire to vaporize and "explode" the wire can be considered an arc discharge. This vaporization technique and the films thus formed has had limited study [227].

Chemical Vapor Deposition (CVD) [1, 228-230]

Chemistry in plasmas occurs naturally with arcing phenomena such as lightning producing the chemical ozone. Von Gurkie, who made the first frictional electricity machine using a rotating sulfur ball, must have created (and smelled) hydrogen sulfide when it sparked in the presence of moisture. The deposition of carbon from spark discharges in hydrocarbon gases was reported by Henry in 1798. In 1802 Sir Humphry Davy used the new voltaic cells to study arc discharges and the generation of compounds in the arc plasmas.

In the 1880s and the 1890s, chemical vapor deposition (CVD) began to be developed in earnest with the goal of strengthening the carbon filaments in the first light bulbs. In 1880 Sawyer and Man deposited pyrolytic carbon by pyrolysis [231] and in 1891 Mond deposited nickel from nickel carbonyl [232]. The hydrogen reduction of metal chlorides on heated surfaces to form metal films was described by Aylesworth in 1896 [233]. Early chemical vapor deposition was performed at atmospheric pressure following vacuum pumping and flushing to rid the system of unwanted gaseous species. The concentration of chemical vapor precursors and reactants was controlled by diluents and carrier gases such as argon and nitrogen. Titanium carbide coatings were developed and commercialized on tools in the mid-1930s by Metallgesellschaft AG. Modern development of thermally driven atmospheric pressure CVD (APCVD) is considered to have begun with Lander and Germer in 1948 [234]. In 1961 Theurer demonstrated the

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deposition of single-crystal (epitaxial) silicon by CVD [235]. CVD reactors are either "cold-wall reactors" where only the substrate and its holder are heater or "hot wall reactors" where a general volume is heated and a "batch" of substrates is coated. A laser was first used for localized heating for CVD in 1973 [236] and presently a laser is used for heating a moving optical glass fiber for CVD deposition.

APCVD is performed at atmospheric pressure and rather high temperatures. Low-pressure CVD (LPCVD) (or sub-atmospheric CVD—SACVD) is performed at pressures of 0.25 to 2.0 Torr in a reaction-rate limited mode [237]. In general LPCVD provides better coverage and less particulate contamination than APCVD. LPCVD (SACVD) is used in the semiconductor industry for depositing doped silicon, compound semiconductors, tungsten metallization and for depositing passivation layers [238]. Pulsed low-pressure CVD, using pulses of reactant into a low-pressure environment, has been used to deposit thin films [239].

Early vacuum deposition from plasmas containing chemical vapor precursors was termed "glow discharge deposition." Later the process was called "plasma deposition" [229, 240], and later still, "plasma-enhanced CVD" (PECVD) or "plasma-assisted CVD" (PACVD). In 1911 von Bolton reported the deposition of seed crystals of "diamond" from "decomposition of illuminating gas (C_2H_2) in the presence of Hg vapors" [241]. The deposition of inert and glossy carbonaceous films on the walls of gas discharge tubes containing hydrocarbon vapors and other carbon-containing vapors was noted in 1934 [242]. In 1953 Schmellenmeier studied plasma-deposited carbon films and discovered the presence of diamond-like structures (diamond-like carbon—DLC) [243]. DLC films can be produced by several techniques [244], including pyrolysis [245], plasma deposition [246], and carbon-ion ("i-C") beam deposition. In 1965 Sterling and Swann discussed the importance of plasmas in decomposition of chemical vapor precursors [247]. When depositing species from a plasma, the molecules are often incompletely dissociated, thus forming a spectrum of molecules and molecular fragments, both neutral and ionized. Combination of fragments increases the number of species in the plasma. For example, in the PECVD of silicon from silane (SiH_4), the formation of Si_2H_6 is thought to play an important role as it is more readily adsorbed on a surface than is silane. Plasma decomposition and vapor phase nucleation can also produce ultrafine particles [185, 248].

In 1971 Reinberg developed an RF-driven, parallel-plate, PECVD reactor that allowed CVD of materials at a lower temperature than was possible by using thermal processes alone [249]. The "Reinberg reactor," Figure 19, is generally operated at a pressure greater than 0.5 Torr and deposits materials such as glass films (phospho-silicate-glass-PSG) and Si_3N_4 (from silane and nitrogen) for semiconductor encapsulation. Plasma-deposited films are also used for depositing optical coatings [250].

Film deposition by PECVD at very low pressures (10–50 mTorr) (LP-PECVD) allows ions from the plasma to be accelerated to high energies. PECVD onto a negatively biased substrate under high-energy particle bombardment was described in the "ion plating" patent of Mattox in 1967 [251].Figure 20a shows figure 6 from that patent. Culbertson and Mattox used this "chemical ion plating" LP-PECVD process for depositing tungsten from WCl_4 in 1966 [252]. Culbertson used the process to deposit carbon and metal carbide coatings on electron tube grids to provide a low secondary emission coefficient in 1971 [253]. Culbertson's arrangement for depositing titanium carbide films from chemical vapor precursors is shown in Figure 21. He also described using a thermal evaporation filament for the metal vaporization. This was the first application of hybrid PVD/LP-PECVD. Later this process became important in hybrid deposition of hard coatings and decorative/wear coatings, such as metal carbonitrides (e.g., Ti-Al-C-N), using a combination of reactive PVD and LP-PECVD

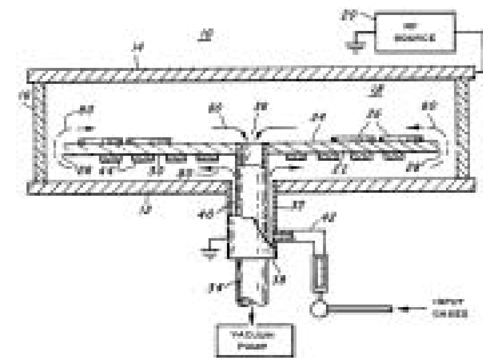

Figure 19. "Reinberg" parallel-plate PECVD reactor (1973) [249].

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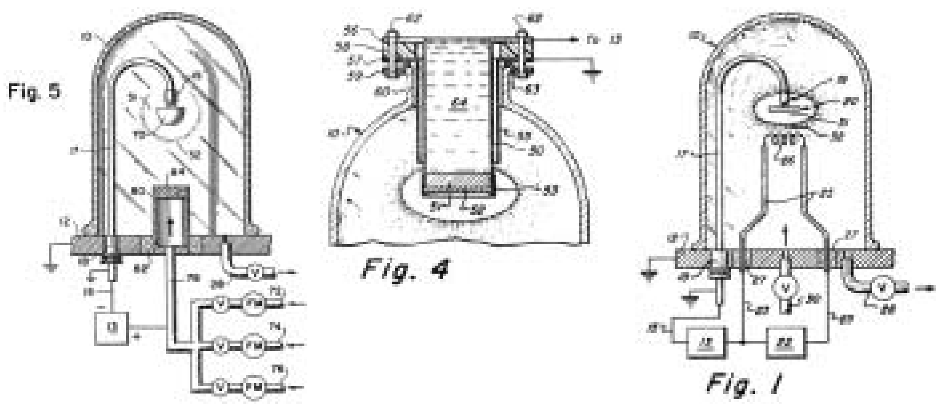

Figure 20. Figures from Marrox's "ion plating" 1967 patent: a) use of chemical vapor precursors in the plasma, b) use of a "cold finger" fixture to keep the bulk of the substrate very cold during deposition, and c) simple un-cooled, un-heated substrate fixture [251].

(see discussion of ion plating). In 1975 Spear and Le Comber showed that the valency of plasma-deposited amorphous silicon could be controlled [254]. This material became the basis of a-Si solar cells (Carlson and Wronski, 1976) [255]. In 1979 LeComber, Spear, and Ghaith reported the development of an amorphous field-effect transistor using amorphous-hydrogenated silicon (a-Si:H) prepared by PECVD of silane (SiH_4) [256].

In 1983 Môri and Namba used methane in a plasma-type ion source to deposit DLC films under bombardment conditions at very low pressures [257]. In the1990s pulsed DC and bipolar pulsed-power PECVD began to be developed [258]. Chemical vapor precursors, at low pressures, are also used in "chemical beam epitaxy" (CBE) [259]. PECVD shares many of the same concerns as "plasma etching," "plasma stripping," and "reactive plasma cleaning." One of these concerns is the pumping of "dirty" and reactive gases, vapors, and particulates through the vacuum pumping system.

Probably the first metal ion beam-type source using the disassociation of a chemical vapor in a plasma was the "Calutron" source developed in WWII [260] (F-13). The Calutron produced ions that were accelerated to 35 kV and magnetically deflected to separate isotopic masses. In 1983 Shanfield and Wolfson formed vacuum-deposited compound films (BN) from a chemical vapor precursor of borazine ($B_3N_4H_6$) injected into a Kaufman-type plasma source [261]. In 2002 Maddocks described a magnetically "pinched" (focused) plasma configuration that may be useful for large-area plasma deposition [261a].

Plasma polymerization (PP) was first noted by de Wilde [262] and also Thenard [263] in 1874. The phenomena was not put into practical use until the 1960s when plasma polymerization was developed to apply thin, pinhole-free polymer coatings on food containers for corrosion protection [264]. Partially oxidized, plasma-polymerized coatings are of interest as permeation barriers and have been plasma-deposited from hexamethyldisiloxane (PP-HMDSO) and hexamethyldisilazane (PP-HMDSN) [265]. The degree of oxidation is determined by controlling the partial pressure of oxygen in the discharge. This type of coating is used as an external vapor barrier on the external surface of three-dimensional plastic containers [266]. Plasma polymerization, along with PVD-type vaporization of solids, are used to deposit mixed metal-polymer "composite" films [267].

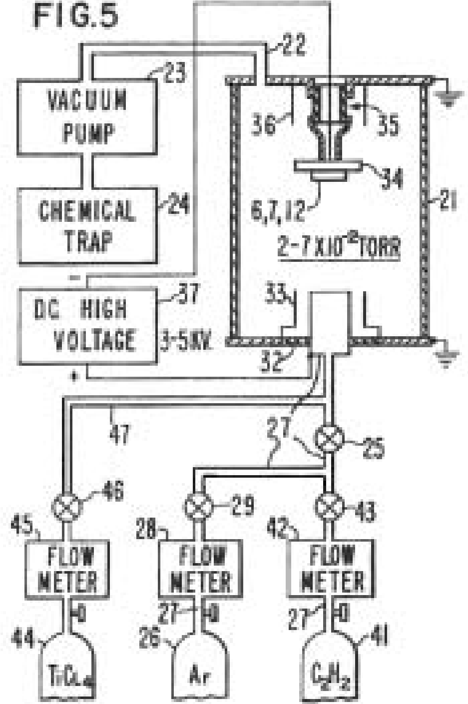

Figure 21. Figure from Culbertson's 1971 patent showing arrangement for depositing titanium carbide films [253].

Electron beam polymerization was observed in the early electron microscopes when hydrocarbon pump oil vapors were polymerized on the specimen by the electron beam. In 1958 Buck and Shoulders proposed the use of electron beam polymerized siloxane vapors as a

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resist in forming miniature printed circuits [268]. Electron beams and ultraviolet (UV) radiation are used to "cure" vapor-deposited organic and inorganic fluid films in vacuum [269].

In the "parylene process" a vapor of organic dimers is polymerized in a hot zone then deposited on a cold surface [270]. The process was initially reported by M.M. Swarc in 1947. The presently used process was developed by W.F. Gorman at Union Carbide beginning in 1952 and was commercialized in 1965 using di-p-xylyene (DXP) at pressures near 1 Torr.

Ion Plating [251-253, 271-277]

In 1963 Mattox described the use of a negative substrate potential on a substrate to obtain ion bombardment from a plasma before and during film deposition [251, 278] (F-14). Bombardment during deposition can be used to modify the properties of the deposited material. Figure 20a shows a figure from the patent that uses LP-CVD. Figure 20c shows the use of a resistively heated evaporation filament. Ion bombardment from the plasma sputter-cleans the substrate surface [279], and by continuing the sputtering while beginning the film deposition, the film-substrate interface is maintained contamination-free.

Initially ion plating used a thermal vaporization source or a chemical vapor precursor or a combination of the two sources. Later, when high-rate sputter vaporization sources were used as a source of deposited material, the process was called "sputter ion plating" by some authors [280] and "bias sputtering" by others. In the ion plating process deposited material may be "back-sputtered" if the bombarding energies are above some "sputtering threshold" energy. Generally this threshold energy is 50 to 100eV depending on the depositing material and mass of the bombarding species ("sputtering yield"). Bombardment below this energy value can modify film properties without having any "back-sputtering" [281]. Generally at low bias potentials high ion fluxes are used to modify the properties of the coating. When depositing compound or alloy materials preferential back-sputtering may affect the composition of the deposit.

To some, ion plating represents a defined deposition process with various vapor sources; to others ion plating is a deposition parameter for deposition processes defined by the vapor source. When using a chemical vapor precursor in a plasma, some authors refer to the process as "chemical ion plating," and it is a low-pressure version of plasma enhanced chemical vapor deposition (PECVD) (see CVD section). The term "ion plating" was first used in 1964 and rationalized by Mattox in 1968 [282]. Some authors prefer the term "ion assisted deposition" (IAD) or "ion vapor deposition" (IVD), or ionized physical vapor deposition (iPVD) and it may also be considered an "energetic condensation" process [283].

Ion bombardment of the substrate and growing film adds thermal energy to the surface region without having to heat the bulk of the material. This allows a sharp thermal gradient to be established between the surface region and the bulk of the material [284]. Figure 20b show the use of a liquid-nitrogen-cooled "cold finger" to keep the bulk of the substrate cold while the surface is bombarded. Figure 20c shows a non-heated, non-cooled substrate holder configuration for ion plating. The ion bombardment also causes atomic rearrangement in the near-surface region during deposition, which increases the film density and intrinsic compressive film stress [285]. The term "atomic peening" for this densification process was first used by Blackman in 1971[286]. Ion bombardment also increases the chemical reactivity between the depositing film material and the co-deposited or adsorbed material [287]. The presence of the plasma "activates" reactive species in the gaseous deposition environment and makes them more chemically reactive with the deposited material ("reactive ion plating").

Mattox also demonstrated that the ion plating process provides good surface coverage over three-dimensional surfaces from a point vaporization source. This is due to scattering in the gaseous environment (10–40 mTorr). The problem of "sooting" [185] was not encountered because the vapor phase condensed particles become negatively charged and therefore are repelled from the negative substrate. Soot deposit on the wall, however, is a problem for system maintenance when high-rate vaporization is used. Attempts to use scattering in the gas phase to improve coverage without a negative bias and bombardment were not

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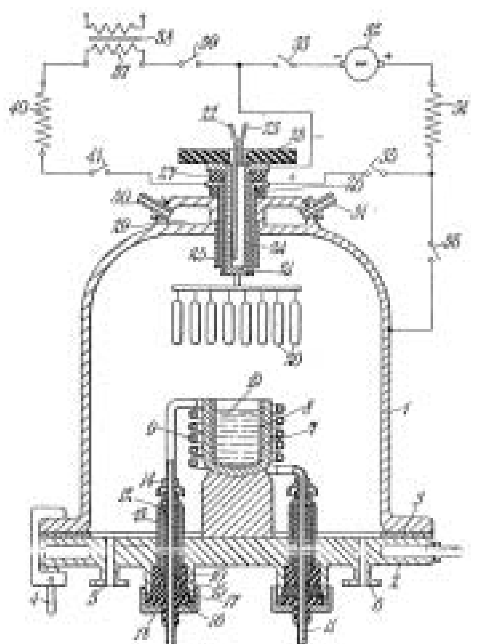

Figure 22. Figure from Berghaus's 1938 patent showing an "ion plating" configuration [289]. This work was overlooked for 25 years.

very successful [288].

A great deal of effort was expended to find "prior art" for the ion plating technology, even though the Mattox patent was in the public domain from its inception since he worked under contract for the United States Atomic Energy Commission (USAEC) (F-5). One prior patent by Berghaus was located. That patent described a similar process that involved coating articles with a negative bias in a glow discharge, as shown in Figure 22 [289]. Berghaus in his 1938 and 1942 patents stated that the coating adhesion was improved and that the coating was densified by the method. No technical papers were found on his process and the technique was not mentioned in L. Holland's book Vacuum Deposition of Thin Films (1961), though Holland referenced other work of Berghaus.

In 1962 F. Wehner patented a process using a triode-sputtering configuration for deposition of epitaxial films [62]. Figure 9 shows his apparatus, which uses a mercury plasma. A paper published in 1962 discussed periodic bombardment of the depositing film using an asymmetric AC potential between the sputtering source and the substrate to improve the properties of superconductor film material by periodic ion bombardment during deposition. Frerichs called this technique "protective sputtering" [290].

In 1965 Maisel and Schaible used a negative substrate bias during sputter deposition ("bias sputter deposition") to improve the purity of sputter-deposited chromium films [291]. They found that oxygen was preferentially back-sputtered from the depositing film, forming a purer metal film. In 1965 Glang, Holmwood, and Furois studied the stress in films formed with concurrent ion bombardment [292]. In 1968 Vossen used an RF substrate bias while sputter-depositing aluminum metallization on silicon devices to improve the "throwing power" into surface features [293]. In 1970 Maissel, Jones, and Standley demonstrated that an RF bias on a sputter-deposited ceramic film would densify the deposit [294]. Reactive sputter deposition under ion bombardment conditions began in 1969 with the work of Krikorian and that of Pompei [295].

The ion plating technology was immediately applied to production applications, including the coating of uranium fuel elements for pulsed nuclear reactors [296], tribological coatings for the space program [297], and aluminum coating of fasteners for the aerospace industry [298]. The latter process was known as the "Ivadizing" process using Ivadizer™ equipment and ultimately the "ion vapor deposition" (IVD) process (F-15). The IVD "specs" are "called out" in many military procurement orders [299]. In 1973 Bell and Thompson reported using ion plating as a "strike coat" for electroplating in order to get good adhesion [300]. In 1962 Mattox and Rebarchik reported the use of a biased rotating "cage" with a high-transmission grid to contain loose parts such as nuts and screws (301). The cage avoided the need to make electrical contact to individual parts and is analogous to "barrel plating" in electroplating. The use of a high-transmission grid structure in front of an electrically insulating surface allows ion bombardment of the surface and any dielectric film growing on the surface (302).

In 1975 Schiller, Heisig, and Goedicke published work on thermal evaporation and sputter deposition in which a small amount of metal was periodically deposited and then exposed to bombardment by energetic ions. A coating was obtained by repetitive deposition and bombardment [303]. This process was called "Alternating Ion Plating." A similar technique was employed by Lefebvre, Seeser, Seddon, Scobey, and Manley in 1994 in a patent for periodic deposition and reactive ion bombardment on a rotating cylindrical substrate fixture (OCLI's MetaMode™) to form a coating of a compound material by reactive deposition [304].

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Electron beam (e-beam) evaporation was developed in the mid-1960s, but initially it was not used for ion plating because the high negative voltage on the filament prevented the source from being used in a plasma where positive ions accelerated to the filament, thus rapidly eroded the filament. In 1971 Chambers and Carmichael [166] avoided that problem by having the beam pass through a small hole in a thin sheet in a section of a plate that separated the deposition chamber and the chamber where the filament was located. This allowed a plasma to be formed in the deposition chamber while the filament chamber was kept under a good vacuum. The plasma allowed the ion bombardment of material being thermally evaporated using an e-beam as well as "activation" of a reactive gas. This e-beam evaporation technique could then be used for the deposition of refractory metals and alloys [305]. A magnetic field can be used to guide electrons to impinge on an electrically isolated surface in order to create a "self-bias" that then attracts ions for concurrent bombardment during deposition [87, 306]. This allows ion plating to be performed on an electrically insulating surface without having to use an RF bias.

The use of a negative potential on a substrate immersed in a plasma is called "plasma-based ion plating." From its inception it was realized that only a small fraction of the evaporated or decomposed chemical vapor precursors was ionized ("film ions"). Several investigators attempted to quantify the number of film ions formed with varying techniques [307]. In some investigations post vaporization ionization of the vaporized material was employed [308]. Post vaporization ionization and acceleration is also used in doping of films grown by MBE [309].

With the advent of arc vaporization (which produces a high fraction of vaporized species) as a source of vapor for ion plating, the effects of "self-ion" bombardment became increasingly important [310]. This bombardment has the advantage that the mass of the bombarding species is the same as the depositing species, thus maximizing the energy and momentum transfer. Both cathodic arc and anodic arc vaporization have been used for ion plating.

When sputtering at low pressures the reflected high-energy neutrals are not "thermalized" and bombard the depositing film with the same effect as ion bombardment. By changing the gas pressure, the amount of thermalizing can be controlled. "Pressure pulsing" has been used to modify the properties of the depositing material in the same manner as ion bombardment [117]. Energetic particle bombardment of the depositing film can result in incorporation of high concentrations of the bombarding gas into the film [311].

If the material is deposited in a good vacuum, the process may be called "vacuum ion plating" [312]. Vacuum ion plating can be done using condensing vapor bombarded by a separate ion source that may use inert or reactive gas (313). This is usually called ion beam assisted deposition (IBAD). The IBAD process has been especially effective in depositing dense coatings for optical coating applications. Bombardment can be done using a beam of condensable "film-ions" from an ion source. In 1969 Aisenberg and Chabot discussed ion beam deposition of elements and compounds using a plasma source where ions of the

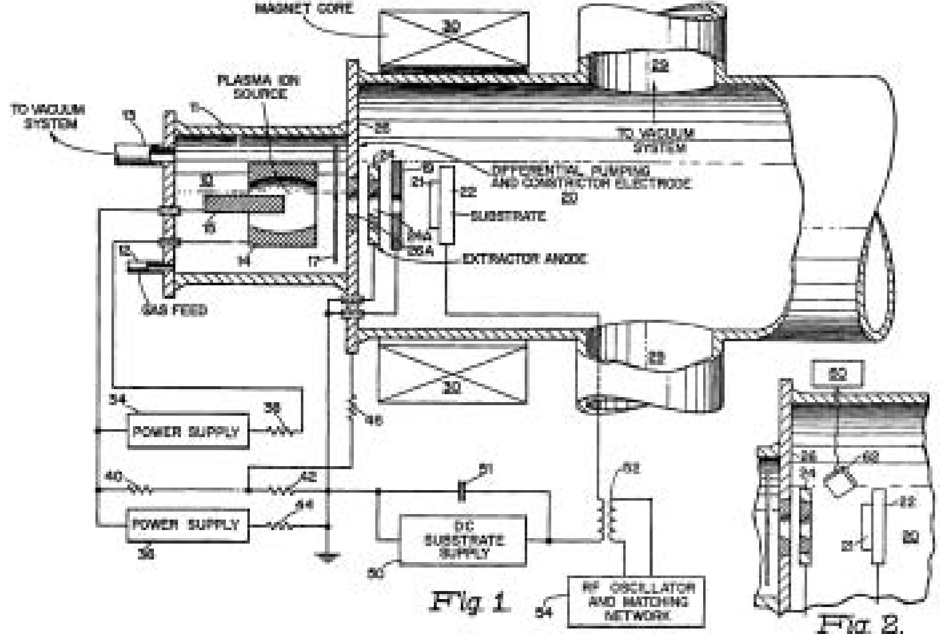

Figure 23. Aisenberg's patent for deposition of DLC material using an ion source from which high energy "film ions" were extracted (1975) [315].

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electrode material (carbon and doped silicon) were extracted into the deposition chamber [314]. When using a pure beam of "film ions" there is no possibility of incorporation of a foreign species in the deposited film. In 1973 Aisenberg used energetic carbon ion (i-C) beams to deposit diamond-like carbon (DLC) material in good vacuum under bombardment conditions [315] (F-16). Figure 23 shows a source from his 1976 patent. The carbon film ions were used to deposit DLC films on plastic lenses and blade edges. Film ions can also be obtained from field emission sources [316]. At high bombardment fluxes and/or energies, "back-sputtering" by gaseous ions [317] or "self-sputtering" by "film ions" [318] can be an important effect. To have appreciable back-sputtering a low flux of high energy ions or a high flux of low energy ions in needed since the "sputtering yield" is a function of the mass and energy of the bombarding particles.

The source of condensable material for ion plating can be a chemical vapor precursor, such as that used in chemical vapor deposition (CVD). Ion-plated tungsten was deposited from WCl_4 in 1966 [252]. Ion-plated carbon (C) and metal (Ti, Cr, Zr, Si) carbide coatings from chemical vapor precursors (e.g., $TiCl_4$ and C_2H_2) were deposited on electron tube grids to decrease secondary electron emission [253]. The carbon coatings were probably what were later called diamond-like-carbon (DLC) coatings. This application was the first use of a combination of PECVD and PVD processes (hybrid process) to deposit metal carbide coatings by ion plating, which is now a common process. In 1974 Mattox discussed the use of reactive ion plating for the deposition of compound films for hard coatings [319].

Periodic bombardment of a substrate surface with very high-energy ion bombardment (>10 keV) is called "plasma immersion ion implantation" (PIII or PI^3) [320] and is similar to a beam-type shallow ion implantation except that it is non-directional. The use of pulsed power prevents the discharge from becoming an arc. If PIII is performed during metal deposition, it is called "plasma immersion ion implantation deposition" (PIIID) [321]. Pulsed plasmas in a high voltage coaxial plasma gun have been used to erode the electrodes and provide the vapor to be deposited. Periodic discharges were obtained by pulsing gas through the tube. For example, Ti(CN) can be deposited using titanium and carbon electrodes and a nitrogen working gas [322].

Surface Preparation (323-324)

Surface preparation is an essential step in nearly all vacuum coating processing and is critical to the nucleation and interface formation steps of the coating process. These "clean" surfaces, in turn, determine the adhesion of the coating, the surface coverage, and—in many cases—the structure and the properties of the resulting deposit. Surface preparation includes not only cleaning but in some cases modification of the chemical, morphological, or mechanical properties of the surface or the near-surface region [325]. These changes can affect the nucleation of the depositing atoms on the surface and the growth of the coating. Cleaning comprises both that done external to the deposition chamber (external cleaning) and that done in the deposition chamber (*in situ* cleaning).

External cleaning for vacuum coating is generally similar to that used in other manufacturing processes of the type called "critical cleaning [323]" or "precision cleaning." Precision cleaning is sometimes defined as "cleaning a surface that already looks clean." A few external cleaning techniques have been developed specifically for vacuum coating or were initially used for vacuum coating. These include ultraviolet-ozone (UV/O_3) oxidative cleaning and sputter (physical) cleaning.

UV/O_3 cleaning was initially developed by Sowell, Cuthrell, Bland, and Mattox in 1974 to clean very fragile quartz-crystal structures that were contaminated with Carnauba wax during grinding and polishing [326]. The cleaning technique was found to be very effective for removing contaminants that formed volatile oxidation products, such as hydrocarbons, from oxidation-resistant surfaces, such as glass, or from surfaces where a coherent oxide was desirable such as silicon. The UV/O_3 environment was also found to create a hydrocarbon-free storage environment for storing cleaned surfaces prior to coating (F-17).

An important aspect of cleaning is to avoid contamination of the surface with particulates. Particulates are a primary cause of pinholes in films deposited on smooth surfaces. In 1960 Willis Whitfield developed the laminar flow "clean bench" that uses a fiber filter to remove

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fine particulates from the air (F-18). The mechanical fiber filter is called a HEPA (High Efficiency Particulate Air) filter and was initially developed for use in filtering the air in mine safety appliances. Initially clean benches and clean rooms were developed to remove radioactive particles and provide clean areas for assembly of contaminant-sensitive components. This was an improvement on the "white rooms" used during WWII.

"Cathodic etching" (preferential sputtering) was probably first used for preparing the surface of metallographic samples for microscopic observation. Preferential sputtering of different crystallographic surfaces delineates the grain structure on highly polished surfaces. The etching also brings out inclusions in the material. This sputtering process cleans the surface, but that is not the purpose of the sputtering in preparing metallographic samples. "Sputter texturing" has been used for creating very micro-rough surfaces by simultaneously contaminating a surface with carbon while sputter etching. The carbon forms islands on the surface that protect small regions of the surface from sputter etching [327]. "Sputter depth profiling" as an analytical technique was developed for use with Auger Electron Spectroscopy in the 1960s.

In 1955 Farnsworth, Schlier, George, and Burger reported using sputter cleaning in an ultra-high vacuum system to prepare ultra-clean surfaces for LEED studies [279]. Sputter cleaning became an integral part of the ion-plating process [271-274] and is now routinely used in the deposition of hard coatings on tools. In 1976 Schiller, Heisig, and Steinfelder reported sputter cleaning of a strip by passing it through the "racetrack" of a magnetron sputtering source [328]. Sputter cleaning has some potential problems such as overheating, gas incorporation in the surface region, radiation damage in the surface region, and the roughening of the surface, particularly if "over done."

Sputtering of the surface of a compound or alloy material can result in the surface composition being changed. Often the species with the least mass [329] or highest vapor pressure [330] is the one preferentially sputtered from the surface. Bombarding of a carbide surface with hydrogen can result is the loss of carbon ("decarburized") [331].

Reactive cleaning uses a reactive gas to form a volatile compound of the contaminant. Reaction may be promoted by heating—for example, "air firing" or with the use of a plasma in a vacuum "reactive plasma cleaning." Reactive plasma cleaning was the first *in situ* cleaning process and was initially used to clean glass surfaces for optical or reflective coatings. This process, using an air (oxygen-containing) discharge, was used by Strong in 1935 before depositing reflective coatings on glass [332]. Strong used this technique for cleaning glass surfaces for astronomical telescopes [141] (F-19). Most optical coating equipment, even if it only uses thermal evaporation, has a "glow bar" that allows the formation of a plasma for plasma cleaning of surfaces.

In 1977 Mattox and Kominiak reported reactive plasma cleaning of metal surfaces withplasmas containing chlorine [333]. Reactive plasma cleaning is also used for *in situ* cleaning of vacuum surfaces in vacuum systems [334] and to "strip" deposits from vacuum surfaces.

A surface in contact with a plasma acquires a negative voltage (several volts) with respect to the plasma. This sheath potential accelerates positive ions to the surface. When an ion contacts the surface it acquires electrons and releases its energy of ionization (5 to 20 eV). This bombardment and heating desorb adsorbed contaminants such as water vapor. This type of plasma cleaning is called "ion scrubbing" [325].

Plasmas are also used to "activate" the surface of polymer substrates either by generating free radicals of surface species or grafting reactive species, such as oxygen or nitrogen, to the surface ("functionalization"). This activation can be used to increase the adhesion of the deposited film to the substrate [335]. Plasmas can also generate electronic sites on ceramics that can affect nucleation and adhesion [336].

The first studies on plasma treatment of polymers was for adhesive bonding. The first studies used corona discharges in air by Rossman [337]. In the late 1960s inert gas plasmas were used in the process called "crosslinking by activated species of inert gas" ("CASING") [338] though the inert gas was probably contaminated by reactive species. Plasma treatment can also be used to crosslink low-molecular species on the surface thus avoiding the "weak boundary layer" adhesion problem. UV radiation from the plasma probably plays an important role in this

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"curing" process.

A substrate surface can be hardened by the formation of dispersion of carbide, nitride or boride phases in the near-surface region. This can be done external to the deposition system by diffusion of reactive species into the appropriate alloy material at high temperature. Dispersion hardening can be done in vacuum by ion implantation [339] or in a plasma by ion bombardment and heating by the reactive species. The term "ionitriding" is used for the plasma nitriding process [340] and "plasma carburizing" for forming a carbide phase [340a]. In "plasma source ion implantation" pulsed plasmas are use to diffuse reactive species into the surface [320].

Vapor deposited fluid films are use to "flow coat" webs in vacuum to cover surface defects and smooth the surface. These polymer films are then cured with UV or electron beam irradiation [269].

The chemistry of a surface can be changed by depositing a "glue layer" such as in the glass-Ti-Au system where the titanium is oxygen-active and reacts with the glass and gold is soluble in the titanium [3341]. In reactive deposition the intermediate layer can be deposited by limiting the availability of the reactive species. For example, the system may be: substrate-Ti-TiN_{x-1}-TiN formed by limiting the availability of the nitrogen. This is called a "graded" interface [341, 342].

Summary

Today there are thousands of applications of the vacuum coating technologies. It is hard to realize that the industry is only about 70 years old. The vapor sources for vacuum coating are 100 to 150 years old but commercial uses did not start until the mid-1930s with the development of thermal evaporation in vacuum.

As with many inventions and inventors [343] (F-20) it is often difficult to establish the originator of any particular idea or invention. The search is complicated by the information being in both the patent and the technical literature. Patents seldom cite relevant technical papers and technical papers seldom cite relevant patent literature. Often there is controversy over aspects of the information provided.

The sputtering phenomenon was widely studied in the 1920s and 1930s (Guentherschulze et al) as well as in the 1950s and 1960s (Wehner [57] et al). Sputter deposition was the first vacuum coating technology to be available, but with the exception of Edison's deposition on thermally sensitive wax substrates and some work on specialized mirrors, the technique was not widely used until the advent of semiconductor device fabrication. The use of encapsulated aluminum metallization on silicon devices revealed the problem of "stress voiding" that could be solved by the use of an Al-Cu-Si alloy metallization [344]. Sputter deposition was the answer.

Applications of sputter deposition increased rapidly after the invention of the various high-rate magnetron sputtering sources in the early 1970s. Reactive sputter deposition of electrically conductive compound materials (such as the nitrides and carbides) for decorative and hard-coating applications began in the early 1980s. Target "poisoning" and surface flashover (arcing) was a problem when reactive sputtering dielectric materials, such as most oxides. The invention of the dual magnetron and pulsed-power sputtering sources in the early 1990s helped alleviated those problems.

Thermal evaporation was an obvious vapor source long before it was studied. Its development was probably inhibited by the high radiant heat loads and the lack of vacuum materials and techniques that could withstand the heat, particularly in a demountable system. As John Strong comments in his book, "Although the evaporation method was known by 1912, it remained obscure, for some reason, long after it should have become a practical 'tool' in the laboratory" [345]. Thermal evaporation began to be developed in earnest after the work of John Strong on the aluminization of astronomical mirrors. Aluminum was one desirable material that could not be electroplated without great danger and difficulty. The technology advanced further with the development of e-beam evaporation that allowed refractory materials to be deposited. Evaporation into plasmas extended the technique into the realm of reactive evaporation.

Arc vapor deposition had sporadic development in the 1970s but really became important in the 1980s with the introduction of the

reactive arc deposition work of the Russians. Arc vaporization is less sensitive to source "poisoning" than is sputtering and has the advantage that much of the vaporized material is ionized. The application of arc deposition became more useful as extended arc sources, such as rods, became available.

Thermally driven chemical vapor deposition (CVD) had limited usefulness because of the high temperatures required. High temperature in general requires that the coefficient of thermal expansion of the substrate and the coating must be matched, or else excessive strains are introduced. The advent of plasma-enhanced CVD lowered the deposition temperature required and PECVD began to be used, particularly in the semiconductor processing industry. At the pressures used for PECVD it was not possible to accelerate ions to high energies. This was overcome by the use of LP-CVD, which was done at "sputtering pressures" (i.e., 10 mTorr or so).

Ion plating utilizes continuous or periodic bombardment by high-energy atomic-sized particles, generally ions, to modify the properties of the deposited material. The bombardment densifies the deposited material and enhances the chemical reactions necessary for reactive deposition. The concept of bombardment during deposition was patented in the late 1930s but was "lost" until the early 1960s. At that time the process was patented using chemical vapor precursors (LP-CVD) and thermal evaporation sources. Sputter deposition at that time was slow and the use of "bias sputtering" (bias sputter deposition) was limited. The advent of magnetron sputtering made the use of concurrent bombardment more attractive.

Even though the vacuum coating industry really began in the mid-1930s (F-21), World War II added an impetus to the development. The applications of vacuum coating are continually expanding as new sources, processes, and requirements develop. For example, optically variable films are becoming more useful for security and anti-counterfeiting applications [346].

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Footnotes

(F-1) To be a "pioneering" work as far as application is concerned, I mean that the work was pursued with "vigor" by the initial investigator or other contemporaries, and that the initial work was recognized by future investigators. The key seems to be that there was a need or there was a marketing operation capable of creating a perceived need, otherwise the work was "lost."

(F-2) One of the first commercial applications of hydroelectric AC was in the mining town of Telluride, Colorado. In 1891, a water-powered Westinghouse AC generator produced power that was transmitted 2.5 miles to power a 100 horsepower AC induction (Tesla) motor at the Gold King mine. This hydroelectric power replaced the steam-generated DC electric power that had become too expensive. The cost of electricity at the mine dropped from $2,500/month to $500/month. Several years later the town of Telluride was electrified. This installation preceded the Niagara Falls hydroelectric AC generating plant that came on-line in 1895.

(F-3) The introduction and use of "pulsed power" brought forth a number of terms such as "asymmetrical AC," "unipolar pulsed DC," bipolar pulsed DC," "counterpulse," and even "bipolar DC." These terms were often not defined by the authors and sometimes flew in the face of accepted usage of electrical terminology.

(F-4) In this time period the term "arts" was used as we use the term "technology" today. The term is still used in the patent literature, e.g., "prior art."

(F-5) The question arises as to why much of the early work done under government contract or by government employees was not patented. Before 1980 the U.S. government employees and contractors were only interested in putting R&D work in the Public Domain because they were not allowed to patent and license the work for profit. In 1980 Congress passed legislation (the Bayh-Dole Act and the Stevenson-Wydler Technology Innovation Act) that allowed work developed with government support to be patented and protected. Patents then became much more desirable at government-owned government-operated (GOGO) and government-owned contractor-operated (GOCO) establishments such as the Rocky Flats Plant. However, the initial work on magnetron sputtering from a hemispherical target was for a classified project.

(F-6) In 1970 John Chapin, John Mullay, and Ted van Vorous—all of whom had worked at the Dow Chemical Co., Rocky Flats Plant—formed Vacuum Technology Associates (VacTec). VacTec had a contract with Airco to develop a long, linear, high-rate sputtering source. Airco provided money and equipment for the development work. Chapin initially used a trough-shaped source similar in cross-section to the hemispherical configuration that Mullaly had used in 1969. He quickly obtained the desired sputtering rate for copper. He also conceived the flat planar design. Luckily he noted the idea in his engineering notebook and that entry was witnessed by Bob Cormia of Airco. It would seem that Corbani's patent "anticipated" Chapin's patent. However Chapin was able to "swear behind" Corbani's disclosure based on the notebook entry and therefore Chapin's patent took precedence and Chapin is credited with inventing the planar magnetron sputtering source. Initially there was disagreement between Airco and VacTec about who owned the patent for the planar magnetron. The disagreement was played out in court with the decision in favor of Airco for

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long sources. Afterward Airco made and marketed long planar magnetron sources and VacTec made shorter versions.

(F-6a) Shorter Oxford Dictionary, 3rd edition (1955)—Sputter v (1598) or sputter sb (1673) also splutter sb (1823)—an English term meaning "To spit out a spray of particles in noisy bursts." Imitative origin from the Dutch word sputteren.

(F-7) L. Holland has the wrong page [p. 546] for ref. 115 in his book (107, reference 2) and this mistake has been perpetuated in several subsequent works.

(F-8) John Strong gives 1928 as the date of Ritschl's work in the text of his book (ref. 124, p. 171), but gives ref. 117 as the reference to Ritschl's work. As a contemporary of Ritschl, Strong could be called the "father of filament evaporation" for his long efforts in this area, so I think that he must have had a good reason for using 1928 as the year of the work.

(F-9) Before the use of aluminizing to coat astronomical front-surface mirrors, chemically deposited silver was used [40]. The silver coating had to be carefully polished but polishing left minute scratches that limited the resolution of the mirror. For example, with a silver coating on the 100" Crossley reflector telescope at the Lick Observatory the companion star to Sirius was very difficult to resolve. Using a thin (1000Å) aluminum coating, the companion was easily seen [141]. Silver also tarnished with age, reducing the reflectivity. Aluminum, on the other hand, forms a protective oxide coating and the reflectivity remains constant. In some cases an SiO coating is applied for additional protection.

(F-10) "One of the men working for Wright was an amateur astronomer who had trouble with silver wearing off his telescopic mirror. In their lab was a machine that could vaporize aluminum so they tried coating one of his mirrors in 'that vaporizing machine.' Wright was so inspired by the results that he immediately began work on a reflector lamp. A glass custard cup was purchased at the dime store, coated with aluminum and a filament rigged up. For the lens a curved section was cut out of a giant incandescent lamp. It didn't take long to realize his idea was indeed a good one." (Quoted from [129]).

(F-10a) After WW II the Japanese camera makers (Canon and Nikon) infringed on many German camera patents. When the Germans complained, the Allied Control Commissions for both Germany and Japan took no action. This allowed the Japanese to rapidly build up their camera industry to the dismay of the Germans. (Information from "Post War Camera & Lens Design Thievery" by Marc James Small <teachnet.edb.utexas.edu/~leica/thievery>)

(F-11) There is some question about the amount of gas phase nucleation that occurred in Takagi's nozzle-expansion technique. It would seem that many of the effects reported by Takagi were due to accelerated ions, not accelerated atomic clusters.

(F-12) When an American jeweler, J. Filner, who was visiting the USSR, noted the gold color of arc-vapor-deposited TiN, he brought the process to the United States in about 1980. (From [33]).

(F-13) The "Calutron" was named for the University of California where the source was developed. The source used a confined plasma to dissociate UCl_4 to provide metal ions of U^{235} and U^{238}, which is the dominant uranium isotope. The ions of the isotopes were then magnetically separated to give "enriched uranium" (U^{235}). The design of this source was considered classified for many years after WWII.

(F-14) Mattox conceived of the ion plating process while discussing the adhesion of metal films to metal with proponents of the theory that diffusion was necessary for good adhesion. Mattox maintained that a clean surface (interface) was a sufficient criterion. Mattox knew that sputter cleaning was being used to produce atomically clean surfaces in ultra-high vacuum for low-energy electron-diffraction (LEED) studies. Using what became the ion plating process, Mattox demonstrated good adhesion between silver films and iron substrates—iron and silver have no solubility even in the molten state. Later silver (a low-shear-strength metal) on steel bearings for solid-film tribological use became an important application of ion plating.

(F-15) Ivadizer™ is the trademark of the McDonnell Douglas Corp., which marketed the equipment for many years as well as coating production parts themselves.

(F-16) The term "diamond-like carbon" (DLC) was first used by S. Aisenberg in 1972 [271]. Some authors use this term to describe hard carbon films with a low hydrogen content, and the term "diamond-like hydrocarbon" (H-DLC) films for hard carbon films containing appreciable hydrogen [F-16-1]. The term "i-C" has also been used for ionized and accelerated carbon ions [F-16-2]. The term "a-C" is used for amorphous carbon. Metal-containing DLC coatings were developed in the mid 1980s for tribological coatings [F-16-3] and are designated Me-DLC. Metal-

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containing MoS_2 coatings had previously been used in tribological applications.

[F-16-1] "Carbon Thin Films," J.C. Angus, P. Koidl, and S. Domitz, p. 89 in Plasma Deposited Thin Films, edited by J. Mort and F. Hansen, CRC Press (1986)

[F-16-2] C. Weismantel, C. Schûrer, R. Frohlich, P. Grau, and H. Lehmann, Thin Solid Films, 61, L5 (1979)

[F-16-3] H. Dimigen, H. Hübsch, and R. Memming, "Tribological and Electrical Properties of Metal-Containing Hydrogenated Carbon Films," *Appl. Phys. Lett.,* 50, 1056 (1987)

(F-17) One of the first experiments on using UV/O_3 cleaning involved using a "black light" purchased at a mineral store. A clean glass slide (clean as determined by a "water drop wetting angle" test) was placed on a stainless steel bench top in the lab. The black light (UV source) was placed over it and the wetting angle monitored for several weeks. No change was found. The control slide, with no black light, showed wetting angle increases within the first hour. Recontamination was by adsorption of vapors from the atmosphere.

(F-18) "Clean bench" or "clean room" is somewhat of a misnomer in that the air is generally only cleaned of particles and ***not*** vapors. In rare cases activated carbon filters are also used to remove vapors.

(F-19) When preparing to aluminize the Palomar mirror, John Strong notified the mirror polishers that he would be using a new cleaning technique using "a special fatty acid compound with precipitated chalk." When he arrived the "special fatty acid compound" was Wild Root Cream Oil hair tonic (ad jingle—"You better get Wild Root Cream Oil, Charlie; It keeps your hair in trim; Because it's non-alcoholic, Charlie; It's made with soothing lanolin"). He stated, "In order to get glass clean you first have to get it properly dirty." The oil residue was "burned-off" using an oxygen plasma in the vacuum deposition chamber. (from [141]).

(F-20) Rev. Hannibal Goodwin was a pastor who developed the flexible photographic film in 1887 to replace glass-plate negatives and make it easier to photograph travelogues to holy sites. Eastman Kodak worked to prevent his patenting the idea until 1898 when Rev. Goodwin was granted his patent. After that Kodak infringed on the patent and the litigation was not settled until after WWI in favor of Ansco ($5M) who had bought the patent rights after Goodwin was killed in a street accident in 1900.

(F-21) In 1936 the company Evaporated Metal Films was formed in Ithaca, New York, by Dr. Robley Williams, John Ruedy and Joel Ufford, all of Cornell University. This company is still in business as a privately held company and is probably the oldest "contract coating" firm performing vacuum coating in the USA.

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